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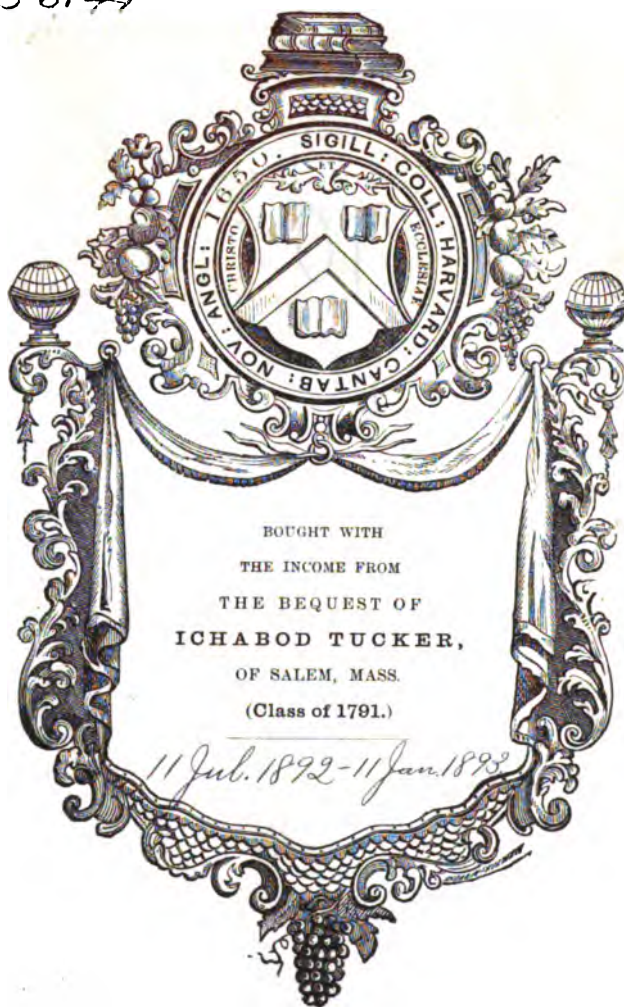
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WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO
PHARMACY, ARTS, AND MANUFACTURES.

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WILLIAM CROOKES, F.R.S., &c.

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Edited by
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(WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE")

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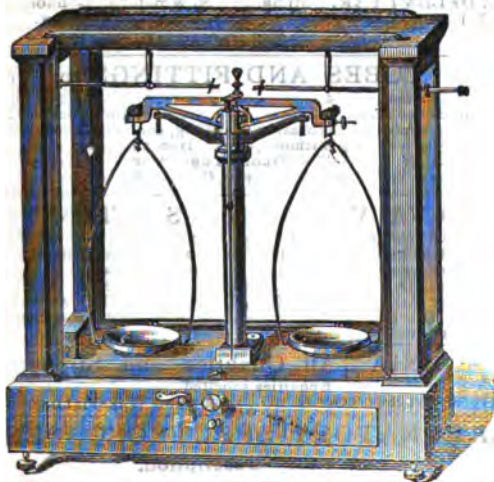


FIG. 3A.

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THE CHEMICAL NEWS.

VOLUME LXVI.

EDITED BY WILLIAM CROOKES, F.R.S.; &c.

No. 1701.—JULY 1, 1892.

A CENTURY OF WORK ON THE DEVELOPMENT OF LIGHT FROM COAL-GAS.*

By VIVIAN B. LEWES, F.I.C., F.C.S.,
Royal Naval College.

THE hundred years which have elapsed since Murdoch made his greatest discovery, and illuminated his house at Redruth with coal-gas made in an iron kettle, has taught us many lessons; and by no means the least important chapter in the history of the century is the rapid growth in our methods not only of making gas but of burning it.

In spite of all that has been learnt, we are only on the outskirts of a true knowledge of the changes which give us our great gaseous illuminant; and although a century of experiment has taught our gas managers the best coal to use, and the best methods and temperatures for producing gas from it, still we are ignorant of the exact nature of the hydrocarbons present in the coal, which, under the influence of destructive distillation, yield the gas, and also of the changes which result in the complex residue we know as tar, and the gaseous mixture which forms the coal-gas itself. The questions still to be answered with regard to coal-gas will take long years of research for their elucidation, and I propose to-day to devote myself to a discussion of the methods we employ for the generation of the light from the gas, and to the facts we have learnt as to the causes of luminosity in flames, rather than to trespass upon a subject which still contains so many unknown factors.

When, in 1792, Murdoch first made coal-gas in his Cornish home, he burnt it as it escaped from the open end of a pipe, but quickly perceiving that a spreading of the flame gave a better light with a decrease in consumption, he fitted a thimble over the end of his tube, and by boring small holes in the thimble head caused the gas to burn in several small jets; but as his experiments progressed the form of his burner was modified, until in 1807 when fitting up the works of Messrs. Phillips and Lee at Manchester, he used two forms of burner,—the one a rough Argand, and the other "a small curved tube with a conical end, having three circular apertures or perforations of about a thirteenth of an inch in diameter, one at the point of the cone, and two lateral ones through which the gas issued, forming three divergent jets of flame somewhat like a *flair de lys*."† This latter burner, which, from the shape of the jet, got the name of the cocksput burner, gave a light equal to two and a quarter mould candles of six to the pound, whilst the Argands used

developed a light equal to four candles of the same description.

The Argand burner had been in use for the consumption of oils for some years before the introduction of coal gas, and in its early form consisted simply of two concentric tubes fixed at the required distance apart, the coal gas being fed in between them. Soon, however, the idea arose of closing the open circular slot by a metal ring pierced with holes so as to give a circle of small jets, and even prior to 1816 the main principles of our present Argands were to be found in the burners then in use.

It was about 1816 also that the cocksput burner became converted into the cockscomb, and then into the batswing, this marking a distinct advance in the method of burning the gas; as by spreading the flame out into a thin sheet instead of having it in a solid mass as in the jet burner, the air was more uniformly and readily supplied to the burning gas, and the increased temperature of the flame due to the more perfect combustion increased the light-giving power of the burner to nearly that of the Argands then in use.

In 1820 Neilson, of Glasgow, whose name will be always remembered as the discoverer of the hot blast in iron-smelting, found that by allowing two flames to impinge upon each other, an increase in luminosity was obtained, and after several preliminary stages the union jet or fishtail burner was produced, in which two holes bored at the necessary angle in the same nipple cause two jets of gas to impinge upon one another so that they mutually splayed themselves out into a flat flame. The shape of the batswing flame was a very wide flame of but little height, whilst the fishtail flame was much higher and narrower, and although the service yielded by the batswing for each foot of gas consumed was no better if as good as that given by the batswing, yet its shape, which made it less affected by draughts, and enabled a globe to be used with it, ensured a greater amount of success for it than the batswing burner had secured.

The next twenty years was a period of improvement and gradual perfecting of the Argand and flat-flame burners, the influence of pressure and regulation of the flow of gas to the burner being gradually realised and allowed for, whilst other structural improvements were introduced later by Sugg, Bray, and others.

In 1854 a new and important departure was made by the Rev. W. R. Bowditch, who conceived the idea of utilising heat, which otherwise would have been lost, to raise the temperature of the air supply by enclosing an Argand burner by a double glass chimney so arranged that the air had to pass down between the glasses, and in its passage became highly heated. The burner itself was never a commercial success, as the high temperature so rapidly

* The Murdoch Lecture; Incorporated Gas Institute, June 15, 1892.
† Murdoch's Royal Society paper, 1808.

acted upon the inner glass as to render its frequent renewal necessary, but it marks an important era in the history of lighting by gas, as in it we find the germ of the regenerative lamps, which during the last thirteen years have revolutionised the methods for the production of high illuminating values from gas.

The first successful application of the principle was by F. Siemens in 1879, and the results he obtained were so far in advance of any previous result that others followed in his footsteps, and Clark, Grimston, Bower, and Thorp all contributed burners in which the same principles received slightly different application, and these in turn have given rise to the host of others which not only add to our power of illumination, but also threaten to increase business in the Law Courts.

About the same time that the regenerative burner was struggling into prominence, Mr. Lewis brought out a burner in which the coal-gas was burnt, mixed with air as in a Bunsen burner, and the flame was then urged by an artificial blast against a cone of fine platinum wire, which being heated to incandescence, gave a very high candle power per cubic foot of gas consumed, and this proved the forerunner of the Welsbach, Clamond, and other incandescent lights.

Having traced the gradual genesis of our present burners, we must now glance at the theories which have been from time to time advanced as to the causes which endow a flame containing those compounds which we know as hydrocarbons with the properties of emitting light, as until we have some conception of the causes which give rise to luminosity in a flame, it is impossible to arrive at any idea of how far further improvements may be expected to go, and in what direction to look for them.

Whilst this century was still in its teens Sir Humphry Davy undertook his great research which culminated in the invention of the Davy safety lamp, and during that great work he made some observations which led him to further researches upon the cause of luminosity in flames, which were embodied in his historical paper published in the *Transactions* of the Royal Society for 1817.

These researches led him to the conclusion that the luminosity of flames is due "to the decomposition of part of the gas towards the interior of the flame where the air is in smallest quantity, and the deposition of solid carbon which, first by its ignition and then by its combustion, increases in a high degree the intensity of the light."

Davy's explanation remained unquestioned until 1868, when Dr. Frankland showed that flames such as those of hydrogen in oxygen could be rendered luminous by compressing the oxygen, and that such a flame contained no solid particles as required by Davy's theory, also that the intense light emitted by phosphorus burning in oxygen, or arsenic in oxygen, could not be due to this cause, as the temperature of the flame was higher than the volatilising point of the products, phosphorus pentoxide and arsenious trioxide. The combustion of phosphorus in oxygen, for instance, giving a temperature of over 1300° C., whilst the oxide formed volatilises at between 800 and 900° C.

Dr. Frankland's research proved beyond doubt that a flame containing dense vapours might be luminous, but he failed in proving, as he claimed, that the luminosity of a coal-gas flame was due to dense hydrocarbon vapours heated to incandescence, and not as Davy had stated to separated carbon particles at a high temperature. This paper gave rise to a large number of other researches and communications on the subject, which largely increased our knowledge of the actions going on in flames and the various causes which affect them.

Dr. Frankland not only showed that flames might be luminous without containing solid particles, but advanced the theory that the luminosity in the flame of a burning gaseous hydrocarbon was due to dense hydrocarbon vapours, and pointed out that the soot deposited upon any cool substance held in such a flame contained

hydrogen. To this W. Stein replied, showing that the deposited soot contained less than 1 per cent of hydrogen, which was therefore probably only occluded by the carbon; and also that, if it had been present as a vapour in the flame, it ought, on being heated to the same temperature as the flame, to be once again volatile, which it undoubtedly is not. In the year 1874 Soret attempted to show that the cause of luminosity in flame really does depend upon the presence of solid particles, by focussing the sun's rays upon a luminous flame, and examining the reflected light by means of a Nicol prism; and rather later Burch pursued the same line of research, but employed the spectroscope for his examination of the reflected light, whilst quite lately Prof. Stokes by the same line of research has confirmed their results, all of which point conclusively to the presence of solid particles in those flames which owe their luminosity to the combustion of hydrocarbons. Heumann also in 1876 pointed out that hydrocarbon flames gave a distinct shadow, which is only the case when solid particles are present.

It is impossible to gainsay or refute the mass of evidence which has been adduced upon this point, and we must accept as proved beyond doubt that the luminous portion of hydrocarbon flames contains solid particles of practically pure carbon, which partly by their own combustion and partly by the combustion of the other gases present, are heated to incandescence and contribute at any rate a very large proportion of the luminosity of the flame.

In the present state of our knowledge I should be extremely sorry to say that the luminous portion of a flame does not contain some extremely heavy hydrocarbon vapours, and that these may not under the influence of intense heat add to the general effect, but I have been at present unable to detect their presence, whilst the presence of solid particles has been abundantly proved.

Several attempts have been made to trace the chemical changes going on during the combustion of the flame gases, and Hilgard, Blochmann, and Landolt did this by withdrawing portions of the gases from different parts of the flame and analysing them, but no definite conclusion was arrived at as to the actions which culminated in the liberation of the all important carbon particles. For some time past I have devoted myself to this point, and with the aid of my assistants have, I think, found the key to the actions which are going on within a luminous flame, actions far more complex than were imagined or provided for by the older theories and yet in themselves beautifully simple.

In our coal-gas we have a mixture of hydrocarbon gases and vapours diluted with hydrogen and small quantities of carbon monoxide, whilst such unwelcome impurities as carbon dioxide, nitrogen, and oxygen also exist in traces as small as the gas manager's skill can make them.

The composition of coal-gas varies considerably with the temperature at which the retorting takes place, and the gas made by one company may vary from time to time within fairly wide limits, whilst the composition of the London gas at the present time is a study of considerable interest, as it reveals occasionally signs of the methods of enrichment which are being tried at some of the principal works.

South Metropolitan Gas.

	1890.	1892.
Hydrogen	57.08	52.22
Unsaturated hydrocarbons ..	4.38	3.47
Saturated hydrocarbons . . .	33.99	33.76
Carbon monoxide	2.63	6.23
" dioxide	0.79	0.60
Nitrogen	0.96	3.23
Oxygen	0.15	0.49
	100.00	100.00

In all our gas flames we can trace by the eye two principal zones and at least one subsidiary one. There is the non-luminous zone just above the burner, and above it again is the all important area of luminosity which gives the value to the flame, and between this and the air comes a thin non-luminous mantle which marks the confines of the flame.

The inner non-luminous zone of the flame has always been looked upon as the zone of non-combustion, and but little attention has been paid to it by the chemist, whilst the gas engineer has often yearned to decrease its size and so increase the zone of luminosity, but has so far found that regeneration is the only practical method of doing so, and if we are to increase the amount of light which it is possible to obtain from a gas flame, it is manifest that this portion of the flame offers us the most promising field for research.

My experiments upon flame gases show that as the coal-gas comes from the burner into the air, the hydrogen, on account of its lightness and diffusive power, finds its way to the exterior of the issuing gas and burns first, combining with the oxygen of the air to form water vapour; next in order of rapidity of burning is the methane or marsh gas, which is also the lightest gas next to hydrogen present; the hydrogen in the marsh gas burns to water, whilst the carbon burns partly to carbon dioxide and partly to carbon monoxide, according as the marsh gas molecule at the moment of combustion is in an excess or deficiency of air.

The carbon monoxide is generated in the flame, partly by incomplete combustion and partly by the action of water vapour on some of the heavy hydrocarbons, so much more rapidly than it is burnt, that it rapidly increases in quantity up to the top of the non-luminous zone.

The combustion of these two gases on the exterior of the lower portion of the escaping coal-gas creates intense heat, and bakes the remaining portions of the gas in the non-luminous zone, and causes important changes to take place in the heavier saturated and unsaturated hydrocarbons present. These consist chiefly of ethylene, benzene, propylene, butylene, and crotonylene, as representatives of the unsaturated hydrocarbons, and methane, ethane, propane, and probably butane, as the saturated.

With the exception of the methane these hydrocarbons are all of considerable density, and the denser they are the smaller is their tendency to find their way to the exterior of the flame, and only the straggling molecules from their ranks do this, so these bodies decrease far more slowly in the earlier portion of the flame than the lighter gases with which they are mixed.

These hydrocarbons, however, are gradually altered by the heat to which they are subjected, and all show a tendency to break up into acetylene at a temperature of a little over 1000° C. (2120° F.), so that by the time the top of the non-luminous zone is reached, 81 per cent of the still existing hydrocarbons have been converted into this body, and the luminosity of the flame commences immediately after.

Acetylene is a clear colourless gas, with a strong and disagreeable odour. It consists of 24 parts by weight of carbon, combined with 2 parts by weight of hydrogen. It is one of those bodies which, during their formation, take in heat instead of giving it out; and it is therefore called an "endothermic" compound. Such substances are especially liable to decomposition, as this is accompanied by a rise in temperature instead of, as is the case with most decompositions, an absorption of heat. Acetylene is decomposed at between 1100° C. and 1200° C. into carbon and hydrogen, together with traces of higher hydrocarbons; while Berthelot has shown it to be so unstable that it can be broken up into carbon and hydrogen by detonating a percussion cap in it.

(To be continued.)

A METHOD FOR THE QUANTITATIVE SEPARATION OF BARIUM FROM CALCIUM BY THE ACTION OF AMYL ALCOHOL ON THE NITRATES.*

By P. E. BROWNING.

THE fact that strontium can be separated quantitatively from calcium by boiling the nitrates with amyl alcohol, as I have recently shown,† naturally suggested a similar separation of barium from calcium by the same general treatment. Solutions of specially purified barium and calcium nitrates were prepared and standardised either by the evaporation or filtration of definite portions after treatment with sulphuric acid. The mean of several closely agreeing results, both by evaporation and filtration, was taken as the standard. The method followed was essentially the same as described in the method for the quantitative separation of strontium from calcium referred to above. The first series of experiments was directed toward an investigation of the action of amyl alcohol upon barium nitrate alone. Accordingly, definite amounts of the barium salt were measured into Bohemian beakers of about 100 c.m.³ capacity and weighed. The water was then evaporated over a water-bath, and the dry salts dissolved in a few drops of water and boiled with 30 c.m.³ of amyl alcohol, that amount being determined upon as convenient, until the normal boiling-point of the alcohol was reached—128° to 130° C. During the boiling the beaker was placed upon a piece of asbestos board about 15 c.m. square to keep the inflammable fumes of the alcohol from the flame. When the temperature of the alcohol reached its normal boiling-point the beaker was removed and the barium nitrate filtered off upon an asbestos felt in a perforated platinum crucible, the crucible and felt having been previously dried and weighed. The filtration was carried on under gentle pressure, the filtrate being received in a beaker standing under a bell jar upon a ground glass plate. The last traces of barium nitrate were removed from the beaker by washing with small amounts of anhydrous amyl alcohol contained in a wash bottle, previously described, to the mouth-piece of which a small chloride of calcium tube was connected. The crucible containing the barium nitrate was placed in an air-bath and heated to 150° C. The process of heating and weighing was repeated until a constant weight was obtained. Series I. shows the results of these experiments, the barium being calculated as oxide.

Series I.

	BaO taken.	BaO found.	Error.
	Grm.	Grm.	Grm.
1.	0.1040	0.1039	0.0001—
2.	0.1043	0.1043	0.0000
3.	0.0524	0.0522	0.0002—
4.	0.0519	0.0518	0.0001—

These results show plainly enough the complete insolubility of the barium salt in the amyl alcohol; but to confirm them the filtrates of 3 and 4 were evaporated to dryness, ignited to burn off any organic matter from the amyl alcohol, treated with sulphuric acid, heated to low redness, and weighed. The weights in both cases showed the absence of any residue.

Series II.

	BaO taken.	BaO found.	Error.	CaO taken.	CaO found.	Error.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
5.	0.1410	0.1406	0.0004—	0.0112	0.0114	0.0002+
6.	0.1300	0.1301	0.0001+	0.0926	0.0926	0.0000
7.	0.1043	0.1049	0.0006+	0.0741	0.0736	0.0005—
8.	0.0781	0.0781	0.0000	0.0556	0.0554	0.0002—
9.	0.0525	0.0526	0.0001+	0.0373	0.0372	0.0001—

* From the *American Journal of Science*, vol. xliii., April, 1892.

† *Ibid.*, xliii., 50.

Series III.

BaO taken. Grm.	BaO found. Grm.	Error. Grm.	CaO taken. Grm.	CaO found. Grm.	Error. Grm.
10. 0.1304	0.1308	0.0004+	0.0927	0.0921	0.0006-
11. 0.1043	0.1046	0.0003+	0.0371	0.0370	0.0001-
12. 0.1037	0.1036	0.0001-	0.0743	0.0744	0.0001+
13. 0.0783	0.0776	0.0007-	0.0427	0.0422	0.0005-
14. 0.0519	0.0521	0.0002+	0.0369	0.0361	0.0008-
15. 0.0519	0.0512	0.0007-	0.0570	0.0567	0.0003-
16. 0.0261	0.0259	0.0002-	0.0925	0.0925	0.0000

The next experiments were directed toward a separation of barium and calcium nitrates. Definite amounts of a solution of barium nitrate were measured from burettes into counterpoised beakers and weighed as already described; the calcium nitrate was then added in solution and the weight taken again. The water was evaporated, and the dry salts dissolved again in the least possible amount of water and boiled as before with 30 c.m.³ of amyl alcohol. The barium salt was filtered off into a perforated platinum crucible containing an asbestos felt, dried, and weighed as previously described. The calcium was determined in the filtrate in the form of the sulphate by evaporation of the alcohol, treatment with an excess of sulphuric acid, and ignition. Series II. gives the results of this treatment.

In Series III. the effect of a double treatment with the alcohol is recorded: In these experiments, after the first boiling already described, the alcohol was decanted upon an asbestos felt under the conditions previously mentioned, and collected in a beaker placed to receive it. The residue was then dried at a gentle heat over a radiator to remove amyl alcohol; dissolved in a few drops of water, and this solution was treated with a drop of dilute nitric acid to assure the condition of nitrate, and evaporated to dryness. After dissolving in a few drops of water, 30 c.m.³ of alcohol were added, and the boiling repeated. The residue was filtered off upon the felt through which the first portion had been decanted and washed with amyl alcohol, care being taken to remove all particles from the beaker by careful rubbing. The crucible and residue were heated to 150° C. as before and weighed. The results after one treatment are fully as satisfactory as those after the double treatment,—a point which simplifies the method considerably. In the separation of strontium from calcium the double treatment was necessary. The form in which the salts separate suggested a possible explanation. The strontium nitrate separate in plate-like masses, while the barium is much more granular, and therefore less liable to include foreign matter.

Series IV. contains the results of certain experiments directed toward the separation of barium and strontium together from calcium. Definite portions of the three nitrate solutions were measured into counterpoised beakers, and the successive weights taken as previously described. The method of treatment was the same as that described in the double treatment of the barium and calcium salts. The correction for the solubility of the strontium salt was applied (0.001 grm. of strontium oxide to 30 c.m.³ of the alcohol used) in the manner defined in

the paper upon the separation of strontium from calcium. The results are tabulated for the nitrates in the cases in which barium and strontium were treated together, but the errors are also averaged on the oxides for the amounts of barium and strontium nitrates taken in order that they may be compared more conveniently with the results of the previously series.

In experiments 21, 25, 15 c.m.³ of the alcohol were used in each boiling instead of the 30 c.m.³ of the previous experiments, and thus the total amount of the corrections for the solubility of the strontium salt was reduced one-half. In experiments 21, 23, and 25 the calcium was determined by precipitation with sulphuric acid, the precipitate being filtered off, ignited at low redness, and weighed.

The rapidity of execution and satisfactory character of the results of this method of separating barium from calcium seem to place it among good analytical methods.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1892.

By WILLIAM CROOKES, F.R.S.,

and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, June 11th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined, three were found to be very slightly turbid; the remainder being clear, bright, and well filtered.

The character of the water supply to the metropolis during the month of May was not found to differ appreciably from that manifested during the two or three months preceding. The proportion of organic matter present in the water—noticeably low throughout—was found to be just a little higher in the March supply than in that of

Series IV.

Ba(NO ₃) ₂ and Sr(NO ₃) ₂ taken. Grm.	Ba(NO ₃) ₂ and Sr(NO ₃) ₂ found and corrected. Grm.	Error in nitrates. Grm.	Error averaged and calculated as oxide. Grm.	CaO taken. Grm.	CaO found. Grm.	Error. Grm.
17. 0.3941	0.3945	0.0004+	0.0002+	0.0283	0.0277	0.0006-
18. 0.1436	0.1442	0.0006+	0.0003+	0.0568	0.0558	0.0010-
19. 0.3163	0.3152	0.0011-	0.0006-	0.0284	0.0274	0.0010-
20. 0.1978	0.1987	0.0009+	0.0005+	0.0285	0.0280	0.0005-
21. 0.1948	0.1932	0.0016-	0.0008-	0.0833	0.0835	0.0002+
22. 0.1971	0.1971	0.0000	0.0000	0.0830	0.0817	0.0013-
23. 0.1973	0.1960	0.0013-	0.0007-	0.0830	0.0824	0.0006-
24. 0.1959	0.1970	0.0011+	0.0005+	0.0830	0.0819	0.0011-
25. 0.1971	0.1963	0.0008+	0.0004+	0.0834	0.0831	0.0003-

February, but lower again in that of April, and still lower in that of the past month; this statement being applicable both to the Thames-derived and the Lea-derived supplies.

The following Table shows the smallness of the proportion of organic matter present in the Thames-derived supply, taken for illustration, and the successive, but not important, decrease in its proportion during the past three months. With the coming on, however, of any considerable rainfall, a corresponding unimportant increase in the proportion may be anticipated. The maximum proportion of organic carbon met with in any one of the 536 samples examined during the past three months, or 0.188 part in 100,000 parts of the water, corresponds as nearly as may be to a little over three-tenths of a grain of organic matter per gallon:—

	Ratio of brown to blue tint.	Oxygen re- quired for oxidation.	Organic carbon per 100,000.	Organic carbon per 100,000.
	Means.	Means.	Means.	Maxima.
March ..	8.6:20	0.043	0.144	0.188
April ..	5.6:20	0.033	0.125	0.147
May ..	4.7:20	0.029	0.119	0.143

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.

NOTE ON THE DETECTION OF CHLORINE AND BROMINE IN PRESENCE OF IODINE.

By D. S. MACNAIR, Ph.D., B.Sc. (Lond.).

WHEN freshly precipitated moist silver iodide is heated with potassium bichromate and concentrated sulphuric acid no iodine is set free, but the precipitate readily dissolves, forming silver iodate, which is precipitated, along with some silver bichromate, on diluting moderately and cooling the solution. Silver bromide, when treated in the same way, gives silver sulphate—the whole of the bromine being set free; while silver chloride behaves like the bromide, giving free chlorine and silver sulphate.

These reactions furnish an easy method of detecting chlorides or bromides in presence of iodides. It is only necessary to precipitate with excess of silver nitrate, filter off and wash the precipitate, and heat it with powdered potassium bichromate and a little strong sulphuric acid. If any chloride or bromide is present, even with a very large excess of iodide, its presence is easily detected by the evolution of chlorine or bromine.

I am at present making further experiments with a view to determining the delicacy of the reaction and also whether it can be conveniently employed for the quantitative separation of iodine from chlorine and bromine.

The People's Palace Technical Schools,
Mile End Road, London, E.

METHODS OF DETERMINING POTASH.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION
OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

METHOD OF LINDO AS MODIFIED BY GLADDING.

1. *Superphosphates*.—Pulverise the fertiliser (200 or 300 grms.) in a mortar. Boil 10 grms. with 300 c.c. of water for thirty minutes; add ammonia in slight excess and then a little oxalate of ammonia, thus precipitating all phosphate and sulphate of lime, oxide of iron, and alumina, &c.; make up to 500 c.c., mix thoroughly, and filter through a dry filter; take 50 c.c., corresponding to 1 gm., evaporate nearly to dryness, add 1 c.c. of dilute H_2SO_4

(1 to 1), and evaporate to dryness and ignite to whiteness. As all the potash is in form of sulphate, no loss need be apprehended by volatilisation of potash, and a full red heat must be used until the residue is perfectly white. This residue is dissolved in hot water plus a few drops of HCl, 5 c.c. of a solution of pure NaCl (containing 20 grms. NaCl to the litre), and an excess of platinum solution (4 c.c.) are now added. This solution is then evaporated to dryness in a small dish, the residue taken up with a little water sufficient to dissolve it, and strong alcohol added. The precipitate is washed thoroughly with alcohol by decantation and on filter as usual. The washing should be continued even after the filtrate is colourless. Ten c.c. of the NH_4Cl solution prepared as directed are now run through the filter, or the washing may be performed in the dish. This 10 c.c. will contain the bulk of the impurities, and is thrown away. Fresh portions of 10 c.c. NH_4Cl are now run through the filter several times (five or six). The filter is then washed thoroughly with pure alcohol, dried, and weighed as usual. The platinum solution used contains 1 gm. metallic platinum in every 10 c.c.

2. *Muriates of Potash*.—In the analysis of these salts an aliquot portion containing 0.500 gm. is evaporated with 10 c.c. platinum solution plus a few drops of HCl, and washed as before.

3. *Sulphate of Potash, Kainite, &c.*—In the analysis of these salts an aliquot portion containing 0.500 gm. is taken, 0.250 gm. of NaCl added, plus a few drops of HCl, and the whole evaporated with 15 c.c. platinum solution. In this case special care must be taken in the washing with alcohol to remove all the double chloride of platinum and sodium. The washing should be continued for some time after the filtrate is colourless. Twenty-five c.c. of the NH_4Cl solution are employed instead of 10 c.c., and the 25 c.c. poured through at least six times to remove all sulphates and chlorides. Wash finally with alcohol, dry, and weigh as usual.

4. *Organic Compounds*.—In case the potash is contained in organic compounds like tobacco-stems, cotton-seed hulls, &c., weigh out 10 grms., saturate with strong sulphuric acid, and ignite in a muffle to destroy organic matter; then proceed as under (1). To prepare the washing solution of NH_4Cl , place in a bottle 500 c.c. H_2O , 100 grms. of NH_4Cl ; shake till dissolved. Now pulverise 5 or 10 grms. of K_2PtCl_6 , put in a bottle, and shake at intervals for six or eight hours; let settle overnight; then filter off liquid into a second bottle. The first bottle is then ready for a preparation of a fresh supply when needed.

ALTERNATE METHODS.

Prepare the fertiliser as for the Lindo-Gladding method, take 10 grms., boil for ten minutes with 200 c.c. water, and after cooling, and without filtering, make up to 1000 c.c., and filter through a dry paper. If the sample have 10 to 15 per cent K_2O (kainite), take 50 c.c. of the filtrate; if from 2 to 3 per cent K_2O (ordinary potash fertilisers), take 100 c.c. of the filtrate. In each case make the volume up to 150 c.c., heat to 100° C., and add, drop by drop, with constant stirring, slight excess of barium chloride; without filtering, in the same manner, add barium hydrate in slight excess. Heat, filter, and wash until precipitate is free of chlorides. Add to filtrate 1 c.c. strong ammonium hydrate and then a saturated solution of ammonium carbonate until excess of barium is precipitated. Heat. Add now, in fine powder, 0.5 gm. pure oxalic acid or 0.75 gm. ammonium oxalate. Filter, wash free of chlorides; evaporate filtrate to dryness in a platinum dish, and holding dish with crucible tongs, ignite carefully over the free flame below red heat until all volatile matter is driven off.

The residue is now digested with hot water, filtered through a small filter, and washed with successive small portions of water until the filtrate amounts to 30 c.c. or more. To this filtrate, after adding two drops of strong

hydrochloric acid, is added, in a porcelain dish, 5 to 10 c.c. of a solution of 10 grms. of platinic chloride in 100 c.c. of water. The mixture is now evaporated on the water-bath to a thick syrup, or further, as above treated with strong alcohol, washed by decantation, collected in a Gooch crucible or other form of filter, washed with strong alcohol, afterwards with 5 c.c. ether, dried for thirty minutes at 100° C., and weighed.

It is desirable, if there is an appearance of foreign matter in the double salt, that it should be washed, according to the previous method, with 10 c.c. of the half-concentrated solution of NH_4Cl , which has been saturated by shaking with K_2PtCl_6 , as recommended by Gladding.

The use of the factor 0.3056 for converting K_2PtCl_6 to KCl and 0.19308 for converting to K_2O are continued.

ANALYSIS OF MOLYBDENITE, REALGAR, AND ORPIMENT.

By P. JANNASCH and V. WASOWICZ.

SOME time ago one of us had opened up several inorganic sulphides (pyrites, blende, antimonite, copper pyrites), by ignition in a current of oxygen for the purposes of quantitative analysis, and at the conclusion of the work several successful preliminary experiments were made on the use of hydrogen peroxide as an oxidising and absorbing agent in place of bromine-water.

In carrying out the following analyses of molybdenite, realgar, and orpiment, with the use of the former reagent, it was found practicable greatly to simplify and improve the process of ignition.

If the products of combustion are received in bromine-water, the excess of bromine and the hydrobromic acid formed during the reaction must be evaporated away before the sulphuric acid is precipitated, as they have a somewhat solvent action upon barium sulphate. By the use of hydrogen peroxide this loss of time is avoided. For the purposes of technical analysis the volumetric determination of the sulphuric acid by means of decinormal alkali or decinormal barium chloride is generally sufficient.

I.—Analysis of Molybdenite.

The material used was from Altenberg, in Saxony. A qualitative analysis showed the presence of molybdenum, iron, and a gangue stone.

The material, ground to an impalpable powder, was ignited in a current of oxygen in a platinum boat. Glass cylinders were used as receivers; they contained a 3 per cent solution of hydrogen peroxide free from sulphuric acid. As a third receiver we used instead of an Erlenmeyer flask a plain glass cylinder of the same height and width as the two other cylinders. Together we consumed for an analysis 150 c.c. of hydrogen peroxide. The combustion required about 90 minutes. Excessive temperatures must be avoided, as otherwise a part of the molybdic acid may sublime. To obviate this the flames beneath the boat were taken very small at first and were then gradually increased. The tiles of the combustion furnace must not be placed close together, as otherwise there easily occurs a volatilisation of molybdic acid. During the decomposition of the molybdenite white vapours escape into the receiver, and at the other end of the combustion-tube sulphuric acid collects in oily drops. As soon as the combustion is complete, the boat is withdrawn from the hot tube by means of a long wire hook. If it has been properly treated the powder in the boat has a whitish-grey colour without any greenish cast; reddish-black particles must not be present. The boat is weighed when cold, covered with ammonia, and heated for an hour upon the water-bath in a well covered porcelain capsule. The greatest part dissolves, leaving

behind a reddish powder. It was filtered off and washed first with ammonia and then with ammoniacal water. The filtrate was heated on the water-bath to expel ammonia, poured into a beaker and precipitated with a solution of mercurous nitrate. The mercurous nitrate precipitated subsides well; it is yellow, curdy, and very voluminous. After 24 hours the precipitate is filtered off and washed with a very weak solution of mercurous nitrate. The mercurous molybdate, carefully dried at 110°, is removed as completely as possible from the filter; the latter is cautiously returned to the funnel and washed with water containing nitric acid. This filtrate is evaporated in a weighed Rosé crucible on the water-bath, the bulk of the precipitate (which has been set aside) is added, and the whole is reduced to metallic molybdenum in a current of hydrogen according to the directions of Otto von Pfordten (*Zeit. für Anal. Chemie*, xxiii., 413). The precaution was observed to conduct the reduction first for half an hour over a common gas-flame, and then to apply the blast so as to avoid every loss of molybdic acid.

The current of hydrogen should be slow. A powerful ignition for almost two hours was needed before the weight became constant. The metallic molybdenum must have a perfectly homogeneous grey colour, free from yellowish particles.

For determining the residue insoluble in ammonia the reddish powder filtered off is slightly ignited and weighed. When heated in a platinum crucible with concentrated hydrochloric acid a portion (merely ferric oxide) was dissolved, leaving the gangue stone undissolved. In the filtrate the iron was determined by precipitation with ammonia. The gangue, after ignition and weighing in the platinum crucible, was heated with hydrofluoric and sulphuric acid, &c., when from 0.1232 grm. of substance there remained merely 0.0012 grm., so that the portion of the mineral insoluble in acid consists chiefly of quartz.

II.—Analysis of Realgar and Orpiment.

The orpiment was obtained from Tajova, in Hungary; the locality of the realgar was unknown. Only granules very carefully selected were used for analysis. Both minerals are very readily decomposed in a current of oxygen, even at a low temperature, and display the following behaviour. At a gentle heat they first take a dark reddish-brown colour, and melt then to a liquid of the same colour, when they burn very rapidly with a blue flame. Arsenious acid sublimates at the front of the combustion tube, and as far as possible it is driven into the receiver by a movable gas-flame. The formation of oily drops as in molybdenite is not observed, sulphurous acid being exclusively formed. The course of the analysis is the same in both cases.

After the completion of the process the porcelain boat is removed from the tube while still hot, and weighed. When moistened with sulphuretted hydrogen water containing hydrochloric acid, there appears a reddish colour, showing the presence of antimony. The residue from orpiment was only 0.2 to 0.3 per cent, and from realgar only 0.5 to 0.6 per cent, so that the authors could not examine it further quantitatively.

The hydrogen peroxide from the receivers, about $\frac{1}{2}$ litre, was evaporated down to about 140 c.c. in the water-bath, mixed with an excess of ammonia, and the cold solution precipitated with magnesia mixture (1 c.c. = 0.013 grm. MgCl_2), avoiding unnecessary excess. After 24 hours the ammonium-magnesium arseniate was filtered on a sūdion-filter and washed with ammonia (1 part water, 2 parts concentrated ammonia). The washed precipitate is dissolved in little hydrochloric acid, and the solution again precipitated with the addition of a couple of drops solution of magnesium chloride. The precipitate is dried at 100°, carefully removed from the filter, the latter extracted with hot highly dilute nitric acid; the solution is then evaporated to dryness in a weighed Rosé crucible. After adding the main portion of the magnesium precipitate the whole is dried in a slow current of oxygen, at

first at a very low temperature, which is gradually increased, ignited, and weighed.

After the evaporation of the ammonia in the filtrate, and adding 2 c.c. of dilute hydrochloric acid, the sulphuric acid is precipitated with barium chloride.—*Fourn. für Praktische Chemie*, vol. xlv., p. 94.

ON THE INFLUENCE OF THE TEMPERATURE OF COLOURED SOLUTIONS UPON THEIR ABSORPTION-SPECTRA.*

By Dr. H. BREMER.

THE results of spectroscopic measurements, as G. Krüss has shown some years ago, may be affected by fluctuations of temperature which occur during an experiment. It was shown that, according to the temperature, varying values were found for the position of the Fraunhofer lines. This depends on the circumstance that the several parts of the measuring instrument expand unequally on a change of temperature, as also that the glass of which the prism consists possesses a different specific gravity at different temperatures, which affects its dispersive power. In order to measure accurately it is in the first place necessary for the instrument not to be exposed to any great fluctuations of temperature during the experiment, or that the observations are made at a temperature not differing greatly from that at which the apparatus has been standardised for wave-lengths.

As regards the measurement of the absorption-spectra of coloured solutions the results may possibly be affected in another manner, by variations of temperature during the experiment. If the rise or the fall of the temperature of the light-absorbing liquid to the extent of a few degrees affects the position and the intensity of the absorptions in the spectrum to a measurable extent, we must, both in the qualitative and quantitative examination of absorption spectra, always take the temperature of the absorbent liquid into account. If the determination of the coefficient of extinction of a liquid requires a considerable time, we must observe whether within such time the temperature of the solution present in the absorption-cell can be raised by 5°, 10°, or more, by heat radiating from the source of light. To decide this question H. Bremer undertook the following investigation at the instigation of Prof. Krüss.

It is known from a number of instances that the colour of solutions can be affected by the temperature. As far back as 1832 Schoenbein described the changes of colour of certain coloured solutions on heating. He observed that solutions of ferric hydrochlorate or nitrate which had a distinct tint at 20° became colourless at 0°, but had a much darker colour at 50°. Further, a deep blue (?) solution of potassium permanganate if cooled down to -50° became bright red, and was colourless at -100°. Very deeply coloured solutions of chromic acid and alkaline chromates appear of a pale yellow at very low temperatures.

In 1859 H. Schiff examined the solutions of forty salts and observed that with few exceptions they became darker if heated, blue substances least so.

Recently E. Wiedemann observed that the violet solution of iodine in carbon disulphide takes a brown colour if strongly refrigerated, and that brown solutions of iodine in the ethers of fatty acids became violet if heated to about 80°.

Gladstone first observed changes of colour in saline solutions spectroscopically. He examined solutions of ferric chloride, nickelous chloride and iodide, copper chloride and bromide, cobaltous chloride and sulpho-

cyanide, and referred the difference of the spectra of these salts to a change of chemical constitution occasioned by heat. He considers such a change excluded in the following salts, which also show a change of colour: gold bromide, cerium nitrate (red), potassium dichromate, ferrocyanide, and ferricyanide, molybdenum bichloride, platinum and palladium chlorides, and alkaline polysulphides. He observed further that the change of colour lasted only as long as the elevated temperature was maintained. In order to fix the results of this investigation he photographed the absorption-spectra of the above mentioned compounds both at the ordinary temperature and when heated, but unfortunately he recorded no determinations of the temperatures.

Especially interesting are the results of some experiments by Feussner, who submitted the spectra of ferric chloride, copper chloride, copper sulphate, copper-ammonium sulphate, potassium dichromate, nickel nitrate, cobaltous chloride, and platinum chloride to a rather closer examination. In all the solutions there appeared on heating an increase of the absorptive power, and this to a greater degree in chlorides than in other salts.

About the same time Melde observed that the spectrum of carmine, magenta, and aniline blue were independent of temperature, whilst in potassium chromate, picric acid, ferric chloride, and sodium dinitrophenylate a rise of temperature occasioned a qualitative displacement of the absorption from the blue towards the red end of the spectrum.

Similar observations were made a few years later by Houston, Morton, Hartley, Russell, Carnelley, B. Walter, and others.

All previous researches on the influence of temperature upon the colour and the absorbent power of salts have been confined to a description of the changes occurring in their general appearance; exact measurements scarcely exist as yet. The phenomena must be exactly measured rather as not merely qualitative but quantitative spectrum analysis is more and more concerned with the elimination of possible sources of error.

For the measurements there was used a Krüss universal spectral apparatus with a symmetrical double slit, and only the single 60° prism was used. In this manner a strongly illuminated spectrum was obtained; the absorption bands came up very distinctly, as the dispersion was purposely selected moderate.

For the measurements there were selected solutions of such coloured compounds of which it is known that they are decidedly dissociated by heat, or the colour of which, when heated, seems even to the naked eye to undergo a decided change.

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 303.)

The Atomic Weight of Sulphur.

IT is seen that the ratio between the weights of sodic carbonate and sodic sulphate found in each analysis of cupric sulphate forms a valuable check upon the purity of the first substance. Conversely, if we assume the purity of each of the substances and the molecular weight of one of them, we obtain data for calculating the molecular weight of the other. Since sulphur is probably the least definitely determined of the elements involved, the figures may be used with advantage for the calculation of its atomic weight.

* Being Part II. of "Contributions to Quantitative Spectral Analysis," in the *Zeitschrift für Anorganische Chemie*, No. 3.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences* vol. xxvi.

Molecular Weight of Sodic Sulphate.
(Weights reduced to vacuum).

No. of experiment.	Source of acid.	Na ₂ CO ₃ taken.		Indicator.	Na ₂ SO ₄ found.		Molecular weight Na ₂ SO ₄ if Na ₂ CO ₃ = 106.108.
		Grms.			Grms.		
4.	Electrolysis.	1.29930		M. O.	1.74113		142.189
6.	"	3.18620		Av.	4.26790		142.131
11.	Distillation.	1.01750		M. O.	1.36330		142.169
12.	"	2.07680		M. O.	2.78260		142.169
7.	Electrolysis.	1.22427		Av.	1.63994		142.133
17.	Distillation.	1.77953		Phth.	2.38465		142.189
17.	Electrolysis.	2.04412		Phth.	2.73920		142.189
38.	Distillation.	3.06140		Phth.	4.10220		142.180

Average molecular weight of Na₂SO₄ .. 142.169Average omitting Experiments 4, 6, and 7,
which are less reliable than the others 142.181

The first column in this table indicates the original number of the experiment. The data of Experiments 17 and 38 are given for the first time. The second column shows the source of the acid. The third column gives the weights of sodic carbonate taken; while in the fourth are recorded the indicators used in determining these weights, the abbreviations standing for methyl orange, phenolphthalein, or the average of the two. The last two columns contain respectively the weight in grms. and the molecular weight of the sodic sulphate. Since half of the results were obtained with methyl orange, it is unnecessary to correct the result for the trace of impurity in the sodic carbonate.

Subtracting from the averages the quantity Na₂O₄ = 110.106 we obtain two values for the atomic weight of sulphur:—

From the first average .. S = 32.063

" second " .. S = 32.075

Usually accepted value.. S = 32.06

A large alteration in the assumed atomic weight of sodium would of course make very little difference in the result, while an alteration of 1/1000 of its value in the atomic weight of carbon changes the atomic weight of sulphur by only about the twentieth of one per cent. Although it is certain that the results are hardly capable of deciding the present uncertainty in the atomic weight of sulphur, the outcome of the comparison is nevertheless an interesting check upon the work previously described.

The check just mentioned proved that the sodic carbonate contained the normal amount of carbon dioxide, but does not prove the absence of a very small amount of neutral impurity from the salt. Such impurity would have but a slight effect upon the ratio of the weights of the two compounds. It is true that this effect would be to diminish instead of to increase the observed atomic weight of sulphur; but it was thought advantageous to attempt the comparison of the sodic carbonate with some salt having a very different equivalent weight, in order to obtain more light upon this point. Accordingly the material to be investigated was converted with suitable precautions into sodic bromide. In Experiment 39, 1.2198 grms. (in vacuum) of sodic carbonate yielded 2.3665 grms. (in vacuum) of the bromide; or—



Upon its face the result was very satisfactory, but the great hygroscopic power of sodic bromide and various other complications afforded a wide possibility of error; hence the experiment was not repeated. To be of value, any such determination must be made the subject of an especial investigation; and for this, with so remote a purpose as the present one, time was wanting.

The Atomic Weight of Copper.

The calculation of the atomic weight of copper from the amount of metal contained in cupric sulphate which

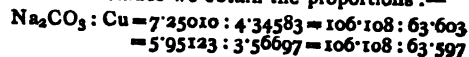
has been dried at 250–270° gives the value 63.35. This result sufficiently approaches Hampe's (63.32) to show the identity of the materials used. But it has been proved that such cupric sulphate still contains a comparatively large amount of water; and this fact renders useless the careful analyses made in 1874. The effect of the correction is considered in a following paragraph.

Besides this method of calculation "from difference," the data which have been given afford twelve other ratios for the computation of the atomic weight of copper. Six of these ratios are useless because of the known error in the crystal water; namely, 5H₂O : Cu;—804.5H₂O : Cu;—5H₂O : CuSO₄;—Na₂CO₃ : CuSO₄.5H₂O;—Na₂SO₄ : CuSO₄.5H₂O;—and BaSO₄ : CuSO₄.5H₂O. Three of these last ratios give values which are much too low, and the other three give values which are much too high, as would naturally be expected. The mean is curiously near to the true value, but need not be further discussed. Neglecting these results because of the known constant error which vitiates them, there still exists seven ratios which do not involve the uncertain amount of the water of crystallisation.

I. From calculations based upon the results tabulated (see p. 303) anhydrous cupric sulphate is seen to contain certainly over 39.807 per cent of copper, and very probably as much as 39.832 per cent. The first number gives 63.53 as the atomic weight of copper, and this value must be regarded as the lowest possible limit. The second—much more probable figure, which takes into account the water held by cupric sulphate at 400°, gives the proportion:—
(CuSO₄—Cu) : Cu = (100.000—39.832) : 39.832 =
= 96.06 : 63.593.

II. From Experiments 4, 6, 7, and 8 it is found that 7.2501 grms. of sodic carbonate correspond to 4.34583 grms. of copper when methyl orange is used as an indicator; and from Experiments 6, 7, and 8 it is found that 5.95165 grms. of sodic carbonate correspond to 3.56697 grms. of copper when phenolphthalein is used as an indicator. It has been shown that the impurities of the sodic carbonate probably rendered the latter quantity of the salt about 0.007 per cent too high; hence the true weight should have been 5.95123. The correction is so small that it has not heretofore been applied.

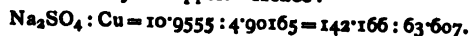
From these values we obtain the proportions:—



Average 63.600

The highest individual result was 63.604, the lowest 63.592, when entirely uncorrected.

III. From Experiments 4, 6, 7, and 9 it is apparent that 10.95552 grms. of sodic sulphate are equivalent to 4.90165 grms. of electrolytic copper. Hence:—



Highest value 63.614

Lowest " 63.595

The last determination (Experiment 9) is by far the most trustworthy. The value deduced from it is 63.600.

IV. From Experiments 4 and 6 it is evident that 4.4855 grms. of sodic carbonate (average) are equivalent to 6.75463 grms. of cupric sulphate which has been dried at 360°. But it is reasonably certain that this cupric sulphate still contained sixty-six hundred-thousandths of its weight of water. Making the appropriate correction we have:—
Na₂CO₃ : CuSO₄ = 4.4855 : (6.7546—0.0044=6.7502) =
= 106.108 : 159.681.

Highest value 159.703

Lowest " 159.673

Subtracting SO₄=96.060, the average value Cu=63.621 is obtained.

V. In the same way, from Experiments 4, 6, and 9, 9.31558 grms. of sodic sulphate are seen to correspond

with $10 \cdot 4715 - 0 \cdot 0069 = 10 \cdot 4646$ grms. of really anhydrous cupric sulphate. Hence:—

$\text{Na}_2\text{SO}_4 : \text{CuSO}_4 = 9 \cdot 3156 : 10 \cdot 4646 = 142 \cdot 166 : 159 \cdot 701$.

Highest value 159'73

Lowest 159'63

From the average, $\text{Cu} = 63 \cdot 641$. This result has a very large probable error, in the chemical as well as in the mathematical sense.

VI. and VII. Only one experiment was made with baric sulphate, but the result is appended for the sake of completeness. From No. 10 it is seen that 100'000 parts of crystallised cupric sulphate are equivalent to 93'289 parts of baric sulphate. But the same amount of the same specimen of the salt had been shown to contain 25'448 parts of copper and 36'109 parts of water. (See vol. lxx., pp. 282 and 303). From these data:—

VI. $\text{BaSO}_4 : \text{Cu} = 93 \cdot 289 : 25 \cdot 448 = 233 \cdot 16 : 63 \cdot 603$.

VII. $\text{BaSO}_4 : \text{CuSO}_4 = 93 \cdot 289 : 63 \cdot 891 = 233 \cdot 16 : 159 \cdot 685$.

From the last value $\text{Cu} = 63 \cdot 625$. The atomic weight of barium probably lies between 137'0 and 137'2; the mean value is assumed above. The corresponding variations of the atomic weight of copper would be from 63'57 to 63'63 with the first ratio, and from 63'54 to 63'69 with the second.

The results of the seven ratios dependent upon the analysis of cupric sulphate are collected in the following table.

The Atomic Weight of Copper.

	Ratio.	Lowest.	Highest.	Experimental mean.
I.	$(\text{CuSO}_4 - \text{Cu}) : \text{Cu}$	[63'53]	[63'62]	63'593
II.	$\text{Na}_2\text{CO}_3 : \text{Cu}$	63'592	63'604	63'600
III.	$\text{Na}_2\text{SO}_4 : \text{Cu}$	63'59	63'61	63'607
IV.	$\text{Na}_2\text{CO}_3 : \text{CuSO}_4$	63'61	63'64	63'621
V.	$\text{Na}_2\text{SO}_4 : \text{CuSO}_4$	63'59	63'67	63'641
VI.	$\text{BaSO}_4 : \text{Cu}$	[63'57]	[63'63]	63'603
VII.	$\text{BaSO}_4 : \text{CuSO}_4$	[63'54]	[63'69]	63'625
Average				63'612
Average, omitting V. and VII. for obvious reasons				63'605

The correction of the experimental mean, in each case, for the amount of copper and sulphuric acid lost during electrolysis, diminishes the variations noticeable above to a remarkable degree. But since the validity of this correction is doubtful, and since its application scarcely influences the two most important results (II. and III.), the figures have been allowed to stand uncorrected. The final average would have remained essentially the same. The highest and lowest values given in this table are in several cases much more seriously in error than the actual experimental results. The reasons for this widening of the limits will be sufficiently understood through a careful perusal of the matter which immediately precedes the table.

Changes in the atomic weights of the elements used as standards of reference of course cause slight changes in the corresponding atomic weights of copper. Sulphur enters into a larger number of the ratios than any other element, excepting, of course, oxygen and copper; but a reasonable change in its assumed atomic weight, while slightly affecting individual results, has no effect upon either of the averages. Carbon and sodium are both determined with a high degree of accuracy, and oxygen is our standard of reference. A fuller discussion of these results will be found in the concluding summary.

(To be continued).

The Reddening of Carbolic Acid.—E. Fabrin (Pharm. Post and Chemiker Zeitung).—According to the author the reddening depends on the action of hydrogen peroxide in presence of metals and ammonia. Pure carbolic acid is not coloured by hydrogen peroxide.

NOTICES OF BOOKS.

Alkali, &c., Works' Regulation Act, 1891. Twenty-Eighth Annual Report on Alkali, &c., Works, by the Chief Inspector. Proceedings during the year 1891 presented to the Local Government Board and to the Secretary for Scotland. London: Her Majesty's Stationery Office.

THIS report is a highly interesting document, satisfactory as showing that the Act is being effectively and judiciously worked, but far from reassuring in the light it throws on the position and prospects of the heavy chemical trades. The total number of works in England scheduled under the Act is slightly increasing, viz., 787 in 1889, 791 in 1890, and 798 in 1891, but the alkali works, strictly speaking, are becoming fewer. In 1890 there were 117 in action, but during last year the number fell to 113. Including Scotland there is a total of 1048 works, 129 of which are alkali works.

The manufactures under inspection are alkali, hydrochloric acid (cylinder process), copper (wet process), cotton carbonising (alkali), sulphuric acid, chemical manures, gas-liquor, nitric acid, sulphate and muriate of ammonia, chlorine and bleaching-powder, sulphur recovery, salt, and cement.

The inspectors have made during the year 4793 visits (which may be made at any time of the day or night, and of which no previous notice is given), and have executed 4863 tests or practical analyses of escaping gases.

It is interesting to learn that manufacturers greatly prefer the Government inspector to the inspector of nuisances employed by the local authority. The maximum quantity of hydrochloric acid permissible in flue or chimney gases is 0'2 grain per cubic foot. Last year the amount actually escaping was only 0'081 grain.

Another requirement of the Act is that of the total hydrochloric acid liberated in any work not more than 5 per cent may escape. The proportion actually escaping is less than one-half of this limit. The total weight of salt consumed in the alkali manufacture in the United Kingdom was last year 846,391 tons. Of this gross amount 567,863 tons were consumed in the Leblanc process, and 278,528 in the ammonia-soda procedure. The latter amount seems growing from year to year.

The annual production of ammoniacal salt is steadily increasing. In 1889 it was 133,604 tons; in 1890 134,257 tons, and last year 143,606 tons. It is obtained as a by-product from gas-works, iron-works, shale-works, and coke and carbonising works. The author even informs us that "there are cases where more of the capital in an iron-smelting work is devoted to the collection and treatment of the tar and ammonia than to the production of the iron itself, and more profit is yielded by the former than by the latter. In some cases iron has become the by-product of an iron-smelting work, yielding the place of main product to the ammonia."

Much progress has been effected in the treatment of vat waste by the Chance-Claus process; 80,000 tons of sulphur have been extracted from this waste at a remunerative figure, and the present yield of 900 tons weekly is valued for its purity. The inspector has been assured that at St. Helens the United Alkali Co. will desulphurise their waste within six months, and at Widnes within twelve months.

As regards chlorine a promising attempt is being made to utilise the oxidising power of nitric acid in place of that of manganese binoxide for decomposing the hydrochloric acid.

It is here justly pointed out that the sulphurous acid which contaminates the air of Widnes and St. Helens is more largely due to the combustion of coal than to the operations of the chemical works. The sulphur converted yearly into sulphuric and sulphurous acids at St. Helens is 36,108 tons, of which only 575 tons is due to the chambers and the alkali-works, and 620 tons to the

Chance-Claus process, whilst the smelting-works and glass-works account for 19,313 tons, and the coal burnt to 15,600 tons. Hence the portion coming within the purview of the Alkali Act is little more than $\frac{1}{4}$ per cent of the whole. In good truth the chemical manufacturer has been made into a scape-goat!

A very sad accident occurred in July last at the Friar's Goose Alkali Works on the Tyne, and proved fatal to seven men, some condensing towers having become dried up and ignited, fell down, burying the workmen engaged. The case was unprecedented, but special arrangements against its recurrence have been adopted by the United Alkali Company.

There is nothing in the Report from which the depressed condition of the cement industry in Kent and South Essex could be inferred. In the latter district one quite new work has come to the hammer, and in others production has been restricted.

A Treatise on Earthy and other Minerals, and Mining.
By D. C. DAVIES, M.E., F.G.S. Third Edition, thoroughly Revised and Enlarged by his Son, E. HENRY DAVIES, M.E., F.G.S. London: Crosby Lockwood and Son.

THIS work, now in its third edition, concerns itself mainly with the non-metallic minerals. We learn from the preface that it has been enlarged by about 60 pp., whilst there have been added about thirty new illustrations. Taken as a whole it decidedly merits the favourable opinion of the technical and scientific press as well as of the public. Certain omissions may, however, be specified in view of a probable new edition. Thus, among the localities for opal, Queensland probably at present occupies the first place. No mention is made under Bauxite of an aluminium terhydrate found at Irish Hill, and admirably suited for the manufacture of aluminous salts. The important deposits of asbestos in Canada might have been usefully noticed.

The account given of the Cheshire and Worcestershire salt deposits and their working in the olden time is extremely interesting. We think, however, that the potassium minerals kainite, carnallite, &c., might have been more fully noticed. We are at present practically limited to one source for these products, and we would suggest that they should be carefully sought for in India and the Colonies.

Comparatively little is said concerning the production of borax in California.

Unless the quarrying of alum shale and the manufacture of alum at Whitby have been lately resumed, they must be pronounced non-existent. When we visited the locality in 1875 we found the quarries forsaken and the works dismantled and falling to decay. The richer deposits of alum-shales at Campsie, near Glasgow, have been abandoned, as in preparing a pure alum the proprietors find it more advantageous to use china-clay or bauxite as a raw material.

As regards the composition of coprolites we may mention finding in a sample a fragment of wood, distinctly characterised by its microscopic structure, but not less rich in phosphoric acid than the accompanying animal remains.

The author's suggestion for the utilisation of the lignite of Devonshire are of the highest importance. As yielding a smokeless fuel in the form of briquettes, it should receive attention now the smoke question is coming to the front.

As a source of sulphur the pyrites from the coal-beds known as "brasses," are available only for the manufacture of ferrous sulphate. Attempts to burn them in the kilns of the sulphuric acid works have proved disastrous. The possible production of arsenic in the world seems largely in excess of the rational demand.

The recently discovered deposit of uranium (uranite) in Cornwall seems to have escaped the author's attention.

The chief defect in this work is one for which Mr.

Davies is in no way responsible. We refer to the lack of precise information concerning the mineral resources of the Colonies. This point concerns us most closely, and it is a matter to be regretted that correct data are not supplied by local geologists, mining engineers, and prospectors.

CORRESPONDENCE.

THE INTERNATIONAL COMMISSION FOR THE REFORM OF CHEMICAL NOMENCLATURE.

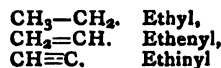
To the Editor of the Chemical News.

SIR,—The whole chemical world must feel themselves greatly indebted to Dr. Armstrong for the admirable explanation of the proposed new arrangements for naming organic compounds, and for the copious illustrations he gave on Thursday, June 16, at the meeting of the Chemical Society.

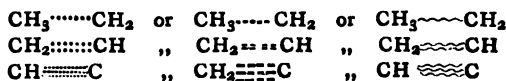
As Dr. Armstrong has ably put forward, doubtless the end and aim of nomenclature is to establish an exact and definite way of speaking and thinking; in fact, to bring chemistry itself, by means of its language, even nearer to a mathematical basis than it is now.

As Professor W. K. Clifford pointed out before the Chemical Society some years ago, the operations to be symbolised, or the methods of aggregation to be thought of and expressed by symbols, have reference to additions and multiplications, but not to the raising of powers; therefore, although the conventions in chemical formulæ are modified and even altered from those accepted and made use of in algebraic formulæ, the expression H^2O or $H^2 + O$ is inadmissible, from its manifest identity in form with $a^2 + b$. Therefore it is very promising to realise that the suffix form— H_2O —is adhered to in chemical symbols.

Since the introduction of bonds to show the combining units of the carbon atom, the signs, —, =, and ≡ have been used in chemical notation, much to the inconvenience of those who have to work with the symbols of pure mathematics as well as with chemical symbols. The identity of these symbols respectively with "minus," "equals," and "is congruent with" is manifest, and the adoption of these symbols as bonds is made more unscientific and unwelcome because equals (=) occurs also in chemical notation. Take—



as examples of these false analogies. Evidently, or ---- (a series of dots or short lines), would be better to indicate the affinities or groupings of molecules; or else a wave line, as suggesting atomic or molecular vibrations. The above would then be—



I also suggest that the use of the word "cycloid" to indicate closed chains is unscientific and is employed without reference to analogy. This word signifies "shaped from a circle, or "by means of a circle," and has been taken in mathematics to mean exclusively the curve generated by a point in the circumference of a circle rolling on a straight line. The cycloid cannot be a closed curve, and has none of the properties of the circle. I propose to use the word "cycle" as more applicable; this word has been employed in astronomy to signify the period of time in which the recurrence of the series of phenomena under discussion begins again, and therefore has relation to a closed condition; one involving all possible changes of place and apparent effects in a given

time—the "cycle" in which lunar eclipses return in very nearly the same order, for instance. If this word be deemed too pedantic, "chains" and "rings" go well together, the ring is the accepted type of closed conditions, and *rings* might have their place more fitly in chemistry than *cycloids*.—I am, &c.,

W. H. WALENN.

9, Carleton Road, Tufnell Park, N.,
June 22, 1892.

SEPARATION OF MANGANESE FROM COBALT AND NICKEL.

To the Editor of the Chemical News.

SIR,—In a recent number of the CHEMICAL NEWS there is an article on a "New Method for the Separation of Manganese from Cobalt and Nickel," by Mr. Paul Jannasch. The process, however, is not exactly new, as I described practically the same method and precautions in vol. lviii., p. 125, and since its appearance I have employed it almost daily with satisfactory results.—I am, &c.,

THOMAS MOORE.

Noumea, New Caledonia, May 14, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 24, June 13, 1892.

At the meeting of the Academy Prof. von Helmholtz was by a large majority of votes elected a foreign associate of the Academy vice the late Dom Pedro d'Alcantara, ex-Emperor of Brazil. It is noteworthy that Dr. Lister, Prof. Nordenskiöld, and Prof. Sir Gabriel Stokes received only one vote each.

Anhydrous Crystalline Nickel and Cobalt Fluorides.—C. Poulenc.—The author obtains at first the amorphous fluoride by the decomposition of the double ammonium fluoride, and then causes it to crystallise in presence of vapours of anhydrous hydrofluoric acid. This method is generally applicable and gives excellent results. Nickel fluoride, NiF_2 , appears in the form of elongated prisms of a fine green. It is almost insoluble in water, and completely insoluble in alcohol and ether. It is not attacked by hydrochloric, nitric, and sulphuric acids, even if hot. Its specific gravity is 4.63. If heated in presence of air it is converted into nickel oxide. Sulphur yields black nickel sulphide. Hydrogen reduces it at a red heat,—a property which the author has utilised for the determination of nickel in the metallic state. The vapour of water decomposes it, with the production of a black oxide retaining the crystalline form of the fluoride. At higher temperatures there is formed green oxide still retaining the same form. Sulphuretted hydrogen converts it at a red heat into a yellow crystalline sulphide and hydrofluoric acid. Cobalt fluoride, CoF_2 , is a rose-coloured powder, very soluble in water. It fuses without volatilisation until it reaches a temperature of 1400°. Its form is that of small ramified prisms. It is slightly soluble in water, insoluble in alcohol and ether. Its specific gravity is 4.43. Hydrochloric, nitric, and sulphuric acid attack it slowly in the cold, but more rapidly in heat.

Action of Nitric Oxide upon the Metals and Metallic Oxides.—Paul Sabatier and J. B. Senderens.—The authors have caused nitric oxide to act at a temperature always below 500°. The gas had been prepared by the action of nitric acid upon a hot concentrated solu-

tion of ferrous sulphate; it was carefully dried and not used until it was perfectly pure. Metals not oxidisable in the air, silver, platinum, &c., are not oxidised by nitric oxide. Liquid mercury, progressively heated to ebullition, remained perfectly bright. Its vapour did not undergo any oxidation even at 450°. Aluminium (in filings) is not altered. The common metals oxidisable in the air, whether taken in a fused state, in sheets or even in filings, are oxidised only very imperfectly in nitric oxide, even if heated to a dull redness: copper, iron, cadmium, zinc are only covered with a superficial layer of oxide. Lead is oxidised more rapidly, forming yellow litharge. It is not the same with metals obtained in a divided state on reducing the oxides by hydrogen; nitric oxide acts upon them at a temperature at which it is perfectly stable, and transforms them entirely into oxides which are usually different from those yielded by oxygen or by air. Reduced nickel heated to 200° in nitric oxide burns with brisk incandescence, yielding greenish yellow protoxide. In air the incandescence is less intense, and the protoxide is always mixed with black sesquioxide. Reduced cobalt, if heated to 150° in nitric oxide, yields maroon-coloured protoxide with lively incandescence. In air we obtain the black intermediate oxide, Co_3O_4 . Iron reduced from the peroxide by a prolonged heating to redness in a current of hydrogen is oxidised in nitric oxide, beginning at 200°. The incandescence is lively, and we have a blackish-grey ferrous oxide. Reduced copper is oxidised in nitric oxide at 200°, and is entirely converted into cuprous oxide, Cu_2O , of a very homogeneous cochineal red. At dull redness incandescence sets in, doubtless primed by a little oxygen which has become free; still the product is identical, but of a more brilliant colour. In air the result is a formation of black CuO . Palladium sponge previously saturated with hydrogen has no appreciable action upon nitric oxide in the cold, but at 200° there is decided incandescence. The nitric oxide is then transformed totally into water and ammonia without any simultaneous oxidation of the metal. The authors have submitted to the action of nitric oxide a number of lower oxides obtained by reducing a higher oxide by means of hydrogen.

Thermo-Chemical Study of Guanidine, of its Salts, and of Nitroguanidine.—C. Matignon.—This memoir does not admit of useful abstraction.

Researches on the Disodium Derivatives of the Three Isomeric Diphenols.—M. de Forcrand.—Also not susceptible of abridgment.

Normal Pyrotartaric or Glutaric Acid.—G. Massol.—The formation-heats of the normal organic diacids are lower than those of their abnormal isomers.

Study on the Decomposition of the Diazo-Compounds.—J. Hauser and P. Th. Müller.—The authors study the influence of the benzenic nucleus on the speed of decomposition.

MISCELLANEOUS.

Appointment.—Dr. A. P. Luff, Lecturer on Medical Jurisprudence and Physician to St. Mary's Hospital, has been appointed Official Analyst to the Home Office in the place of the late Dr. Meymott Tidy.

Deaths from Inhaling Carbonic Acid.—The new chalybeate spring at St. Masitz has demanded in a peculiar manner its sacrifices in consequence of its exceptionally high proportion of carbonic acid. In spite of prohibition three Italians engaged in the buildings penetrated into the closed spring house in order to obtain water for their dinner. The escape of carbonic acid from the well-shaft was so violent that they were stupefied, and notwithstanding immediate assistance two of them died. —*Chemiker Zeitung*.

Certain Laboratory Appliances.—W. Ostwald.—The author describes here small gas furnaces, universal supports, filter-stands and rings, drying furnaces and funnel-holders, sulphuretted hydrogen apparatus, and an excentric latch for the sliding windows of digesting-niches. All these appliances require the accompanying figures.—*Zeitschr. Anal. Chemie*, xxxi., Part 2.

The Naturalists' Society of Switzerland.—The 75th annual gathering of this Association will be held at Bâle on September 5th, 6th, and 7th, and coincides with the 75th year's jubilee of the Bâle Naturalists' Society, and with the meetings of the Swiss Geological Society and of the Swiss Botanical Society. The excursion of the former will be to the Jura, and that of the latter to the Vosges and the Black Forest. The official concluding meeting will be held at the saline springs of Schweizerhall. Applications up to August 20 are to be made to Prof. Fritz Burckhardt, 15, Munsterplatz, Bâle.—*Chemiker Zeitung*.

A Charge against Chemical Works.—Our attention has been called to the following paragraph in the *Medical Press* for the 15th inst.:—"Two men employed in cleaning out a sewer which passed through several chemical works at Widnes succumbed last week to the fumes emanating from the refuse that had accumulated. They had not yet gone into the sewer, but inhaled the gases at the mouth of the open culvert, and before they could move away they were overpowered. It is stated in the local papers that birds have been seen to fall asphyxiated when passing near the culvert." It is not stated what were the dangerous gases. It is of course possible that the drainage from some heap of tank-waste may have found its way into the sewer, and had there encountered some acid solution, giving rise to a liberation of sulphuretted hydrogen.

Determination of the Solubility of Salts.—R. Rüdorff (*Zeit. für Angew. Chemie*).—The arrangement consists of a glass 4 c.m. in height and 2 c.m. wide at the bottom, closed with a cork having two perforations. Through the one passes a narrow glass tube open at both ends, and through the other a short glass tube expanded above the cork, over which is drawn a piece of lawn held fast by a piece of caoutchouc tubing drawn over it. The upper part of this caoutchouc tube is closed by a piece of glass rod. In order to effect a determination a solution of the salt is prepared, saturated at a higher temperature, and the beaker containing the solution is then set in a water-bath of the required temperature. The observer waits until the temperature of the solution agrees with that of the water-bath, the liquid is then stirred up with the apparatus, of which only the glass rod and the narrow glass tube project above its level, and the glass rod is then for a moment drawn out of the flexible tube. A few drops of the solution flow down into the glass. The flexible tube is closed again, the apparatus is lifted up out of the bath, and cleansed by rinsing and wiping. The cork is removed, the glass is closed with a ground stopper, and the solution which has entered is weighed. On determining the quantity of the dissolved body present its solubility is found.

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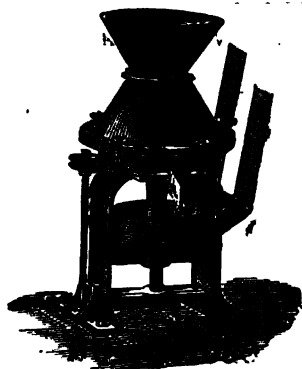
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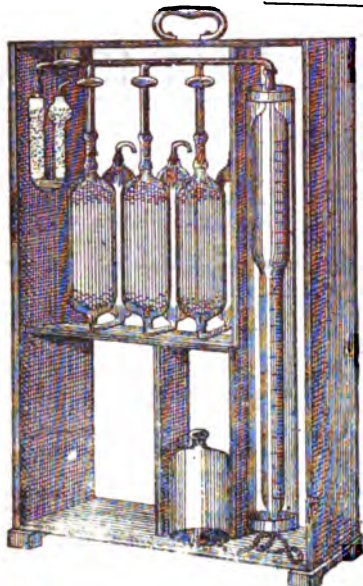
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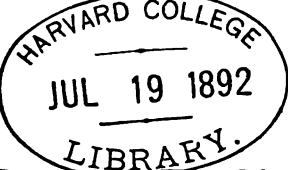
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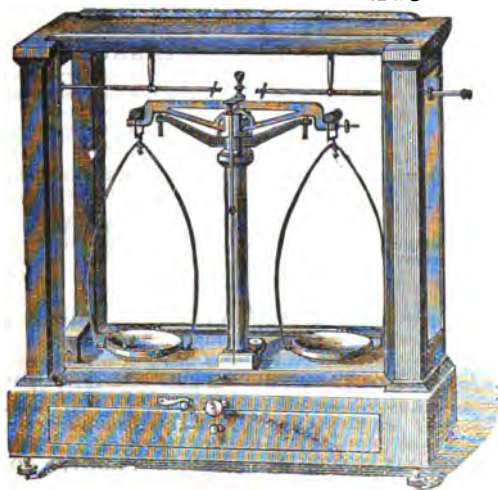


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THE CHEMICAL NEWS.

VOL. LXVI., No. 1702.

THE CONDITION OF THE REACTION BETWEEN CONCENTRATED NITRIC ACID AND METALLIC NITRITES.

By V. H. VELEY, M.A.

IN the course of an experiment made with a view of saturating some concentrated nitric acid as rapidly as possible with nitrogen peroxide, a small stick of fairly dry fused sodium nitrite was placed in about 50 c.c. of the acid (sp. gr. = 1.436, percentage of nitric acid = 70 in round numbers), but after a momentary hissing no further reaction ensued, no nitrous fumes were evolved, and the sodium nitrite remained undissolved. The acid, with the nitrite, was then poured into about the same bulk of distilled water; a violent reaction took place, the effervescence of the nitrous fumes being sufficient to cause the acid to froth over the beaker, which was about half full of liquid.

The experiment was repeated several times and invariably with the same result, thus showing in a qualitative manner that for the reaction between nitric acid and sodium nitrite the presence of a certain proportion of water is necessary. It seems that the experiment above described would form a suitable and easily performed lecture illustration of the presence of water as a condition of chemical change, as also of such a change not taking place except in the presence of an electrolyte (in this case dilute nitric acid); it was thus thought of sufficient interest for the readers of the CHEMICAL NEWS.

Precisely similar results were obtained with dried potassium nitrite and re-crystallised silver nitrite, though the latter case was not so striking.

Another example is added to those already numerous of the well-known aphorism—"Corpora non agunt nisi soluta."

The University Museum, Oxford.

THE BACTERIOLOGICAL EXAMINATION OF WATER.

By DR. MAX DAHMEN.

IT is probably universally recognised that the ordinary method for the bacteriological examination of water has merely a very relative value, and it is therefore not surprising if this investigation is not demanded in all cases. The known method has been elaborated by representatives of medical science, but at present the chemist is in most cases entrusted also with the bacteriological investigation of water. Here may be found a reason why relatively little weight is laid, from a medical point of view, upon the improvement of the method.

The various objections urged against the method are only too well founded. In the first place, the result, the statement of the number of the bacteria found in one c.c. of water, must be inaccurate; because, as Reinsch has shown, it is to a great degree dependent on the proportion of sodium carbonate with which the nutrient medium is neutralised, and, according to the present prescription, only a slight alkalinity is required. But the result depends, not alone on the proportion of soda, but as much on the time allowed to elapse before the enumeration of the colonies and on the species of the micro-organisms. What has been hitherto established is the scarcely approximately accurate number of the bacteria contained in

each c.c. of water, for the most part non-pathogenous. The aquatic bacteria are exactly distinguished by the fact that they are not able to vegetate at the incubation temperature; and consequently have not the property of pathogenic action. These aquatic bacteria are strictly aerobic, and are therefore developed at first only on the surface of the gelatin; the colonies which lie deeper are developed only on the third, fourth, and fifth day, as oxygen penetrates into the nutrient medium. The increase of the anaerobic species is excluded on account of the presence of oxygen, and also because, e.g., the bacillus of malignant oedema begins to vegetate only at 16°, a temperature which does not always prevail in work-rooms. The assertion of Penzo that the bacillus of malignant oedema can vegetate well even with access of oxygen in presence of certain bacteria which are *per se* indifferent, such as *Bac. prodigiosus* and *Proteus vulgaris*, does not come here into consideration, since the bacteria suspended in nutrient gelatin as isolated colonies represent pure cultures. Many other pathogenic bacteria are well known to be incapable of development at the temperature of a dwelling room.

In a bacteriological examination of the water of the Elbe, Reinsch found the optimum condition of growth at about 0.1 to 0.2 per cent of soda in the nutrient medium. For these experiments different quantities of soda were dissolved in lots of nutrient gelatin of 10 c.c. each. For a more accurate result, and to decide whether the optimum condition for growth of bacteria was the same in the water of other rivers, the author experimented on various specimens of Rhine water taken at Oberdingen. The nutrient gelatins were exactly neutralised at a boiling heat by means of soda and neutral tincture of litmus. The optimum degree of alkalinity was found to be 0.1428 per cent of soda. In further experiments, a number of test tubes, each containing 10 c.c. of neutral gelatin, received each two drops of a 10 per cent solution of soda and, in addition, one, two, three drops, &c., of a 2 per cent solution of soda. For the further experiments, the Rhine water was diluted with sterilised water. Here a proportion of 0.15 per cent was found particularly favourable for the bacteria.

In the course of the investigations it appeared that in presence of a great number of the spores of hyphomycetes the numbers of the colonies fluctuated considerably, a circumstance referable to the fact that the hyphomycetes prefer a faintly acid nutrient medium to one which is alkaline. A table has been drawn up showing that the optimum condition of growth of the micro-organisms is displaced by many colonies of hyphomycetes. If the number of colonies of hyphomycetes is subtracted from the entire number of micro-organisms, the optimum condition of growth is given at 0.15 per cent of soda.

It must here be remarked that this 0.15 per cent of soda must not be boiled with the ordinary nutrient gelatin or submitted to prolonged heat, as the nutrient medium otherwise loses the property of gelatinising.

If it has thus been ascertained in what manner the greatest number of bacteria may be found (at least, in the water above named), the question recurs: What is the purpose of knowing the number of the aquatic bacteria, since, as mentioned above, they cannot come to development at the temperature of the body, and cannot in any case become exciters of disease.

If we make use of the double capsules proposed by the author as calculated for the incubation microbe, all those micro-organisms will be excluded from development which cannot vegetate at the temperature of incubation. The colonies of most pathogenic species appear after the lapse of twenty-four hours, and may be further examined at once. These double capsules may be considered as a modification of those of Petri, from which they are distinguished by the circumstance that their hermetic closure prevents at once the evaporation of the moisture of the nutrient agar-agar necessary to vegetation, and protects against contamination by aerial germs.

The water bacteria are twenty and thirty times more numerous than those which vegetate at incubation temperature. We may obtain an approximation to the number of aquatic bacteria by subtracting the number of the colonies of those microbia which grow only at an incubation temperature from the number found by the ordinary plate process. In order to determine more accurately the number of the harmless aquatic bacteria, all the organisms which grow at incubation temperature must be diagnosed, and according as they prosper at the temperature of a dwelling room and are pathogenic, they must be deducted from the total number.

Fränkel writes: "That a drinking water, fit for use, must, above all things, be free from infectious matter has been for many years decidedly demanded by hygiene. It is not merely requisite that waters must be rejected containing bacteria which, though not pathogenic, are saprophytic. I may mention *Bacterium commune coli* (Escherich) and the *Bacillus Emmerich*. If such microbia which are by necessity inmates of the human bowels are present, the uselessness of the water will generally be also shown by chemical analysis.

Suspicious water should always be examined for pathogenic microbia or faecal bacteria, in any case for typhus bacilli. For when an epidemic of typhus has already broken out, the examination of the suspected well merely serves to confirm known facts. A water containing pyogenic microbes is unfit alike for drinking and washing, since if applied to any injured part of the body it may produce suppuration, erysipelas, or even general pyæmia. From the above it appears that a slightly alkaline water does not suffice for bringing out all the bacteria present in a water. A nutrient medium containing 0.15 per cent of soda allows the greatest number of bacteria present in rivers to arrive at development. A suspicious water, even though admissible according to chemical analysis, should be examined for pathogenic and septic organisms, especially for the bacilli of typhus, and rejected if such are present.—*Chemiker Zeitung*.

A CENTURY OF WORK ON THE DEVELOPMENT OF LIGHT FROM COAL-GAS.*

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(Concluded from p. 3).

THE next step in elucidating the cause of luminosity was to determine the temperature existing in the various parts of a flame, and as a flat flame offers a more convenient surface for research than any other, the flame from a No. 7 Bray burner was chosen, and the temperature of the various portions determined by a Le Chatelier thermo-couple.

This consists of a piece of platinum wire, the end of which is twisted with the end of a wire made of platinum with 10 per cent of rhodium. On heating this a galvanic current is generated, and this is made to pass through a reflecting galvanometer of special construction and deflects the needle; a ray of light falls upon a mirror attached to the needle, and is reflected on to a scale so that as the needle moves the spot of light travels along the scale. The scale is graduated into degrees by plunging the thermo-couple into various media the temperature of which is known, and as the current generated is practically proportional to the temperature, it makes a very convenient arrangement for measuring high temperatures.

Using this instrument, it was found that the temperature half an inch above the burner was 500° C. (932° F.), and steadily increased to 1200° C. (2192° F.) at the top of the non-luminous zone, luminosity commencing at

1200° C. (2192° F.). The highest temperature was found to be near the top of the luminous zone, where it reached 1868° C. (2462° F.). In no case is the temperature of the luminous portion of the flame less than from 1100° C. to 1200° C.

Taking the evidence which I have now laid before you, we may, I think, fairly fully explain the actions taking place in the flame and leading to luminosity.

As the gas leaves the jet the hydrogen rapidly diffuses to the outer edge of the flame and burns, the methane doing the same but rather more slowly. The combustion of these gases raise the temperature 500° C. in the first half inch, whilst before another half inch has been traversed 1000° C. is reached, and the chemical changes in the hydrocarbons are progressing rapidly, the unsaturated hydrocarbons and higher members of the saturated hydrocarbons being rapidly converted into acetylene.

If the temperature of the flame was not allowed to rise above 1000° C., this acetylene would be nearly all polymerised into benzene, diphenyl, naphthalene, and other more complex bodies, which would slowly be burnt up without liberation of carbon, and a non-luminous flame would result, as may be shown by holding a platinum dish against a luminous flat flame where luminosity disappears, but may be reproduced by heating the interior of the dish. In the case of a gas-flame, however, instead of remaining at 1000° C., the temperature rapidly rises to 1200° C., and the result is that instead of all polymerising into more complex bodies, most of the acetylene formed at once splits up into carbon and hydrogen, and the former heated to incandescence by combustion gives the luminosity, and it is the attainment of this temperature which marks the limit of the non-luminous zone.

If this were the only action, however, the luminous zone would be very short, but the bodies formed from the acetylene before 1200° C. was reached, and the methane of which some still remains unburnt, are converted into acetylene at a still higher temperature, i.e., 1300° C., and this being reached near the top of the luminous zone, yields a fresh supply of carbon and increases the height of the light-yielding portion of the flame.

In producing a luminous flame, therefore, there are two main factors to be observed, first to use such compounds as shall be most easily converted into acetylene, and secondly, to attain as high a temperature as quickly as possible. The moment we have reached this point in our theory, we naturally think how this can be best done, and find to our disgust that theory has only just caught up practice, as long experience has taught our gas managers that the olefins and unsaturated hydrocarbons are the most valuable illuminants in the gas, whilst our burner makers have slowly and by laborious steps found that by regeneration they can obtain the best results per cubic foot of gas consumed.

Some of my hearers this morning will go beyond this point, however, and it may flash through their mind to ask if acetylene is the key to luminosity, and if this gas is formed by the action of high temperatures on the gas, why is it that retorting at high temperatures gives but a trace of acetylene, and ruins the illuminating power of the gas? Simply because the heat which forms the acetylene also polymerises that body into benzene, and still more largely into naphthalene, especially in presence of carbon; and you know better than I do that high temperatures result in an increased yield of this body, and any attempts to increase the luminosity by superheating the gas must end in failure, as the action taking place in the flame is probably the only method by which this body can be so formed as to yield the desired results. In the flame it is formed and at once decomposed by the heat of the combustion; in the retort it is formed at high heats and yields but traces of benzene and naphthalene, which largely go into the tar or condense where they are least wanted.

Even if it were possible to charge gas with acetylene, it would be useless for practical purposes, as it is soluble

* The Murdoch Lecture; Incorporated Gas Institute, June 15, 1892.

in water and all other media, such as glycerin, which could be used in gasometers and meters; so that once more we come back to the fact that in our gas flame nature has provided the best methods for the carrying on of the actions which culminate in luminosity, and that the most likely field for improvement is in our mechanical treatment of the flame.

This is also shown by the fact that in an ordinary gas flame the luminosity is caused by something like 14 per cent of acetylene liberated at the right spot, whereas double that quantity mixed with a non-luminous gas like hydrogen yields hardly any light-giving power to the flame; because by the time the temperature necessary for the splitting up of the acetylene is reached, it is nearly all burnt up without any liberation of carbon.

Regeneration, as has been before pointed out, increases to a very great extent the light yielded per cubic foot, and this is due to two causes,—in the first place by increasing the temperature, the decompositions necessary to form acetylene and liberate carbon from it are hastened, and so the non-luminous zone is decreased in size and a larger proportion of the gaseous hydrocarbons are converted into acetylene; and secondly by heating the inert nitrogen of the air supply, it prevents the withdrawal of so much heat and raises the carbon particles, when liberated, to a brighter incandescence, and so yields a higher service. Through the kindness of Mr. Siemens I have been enabled to determine the effect of regeneration on a flat flame, both as regards the diminution in size of the inner zone and the increase in luminosity.

The flame when cold had a total area of eleven square inches, of which the luminous zone occupied 7·8 square inches and the non-luminous 3·2; on regenerating this flame the total area decreased to 10·2 square inches, but the luminous zone occupied 7·9 of the space and the non-luminous only 2·3, whilst the illuminating power was increased 100 per cent.

The regenerative burner, however, is by no means the most widely used, and initial cost and domestic inertia are such all-powerful factors, that the flat flame burner is still the burner of the people; and great as have been the improvements effected in this class by our leading makers, the use of the flat flame burner means several millions wasted annually,—not to the profit of the gas manager, but simply in loss of light to the consumer, and as anything which could be done to increase the light-giving power of the flat flame would be an inestimable boon, you will pardon my spending a few moments in pointing out a direction in which I think attempts might be made to do this.

In the passage of the heavy hydrocarbons up the non-luminous zone of the flame a certain percentage must of necessity be lost by wandering into the part of the flame where combustion is taking place, and where they get burnt up without decomposition and so are lost as far as any luminosity is concerned. The larger the inner zone the greater will this loss be, so that if the inner zone can be by any means reduced in size, not only do we gain an increase on luminous surface, but a larger supply of carbon particles to yield light.

Some five and twenty years ago a device for increasing the luminosity of a flat flame called "Scholl's platinum light perfecter" created a considerable amount of interest, and undoubtedly, whilst the perfecter was new, caused a considerable increase in the amount of light emitted by the flame. The perfecter consisted of a thin slip of platinum fixed across the burner and between the orifices of the jet, so that the two streams of gas impinged upon it and afterwards mingled in the flame. The explanation always given of its action was, that in the far from perfect burners then in use, it perfected the combustion of the flame by breaking the rush of the gas, and that had it been applied to a properly regulated burner no gain would have resulted. This view is to a great extent supported by the effects of pressure upon the gain in light obtained by its use, as Mr. Rowden and Capt. Webber found that

the increase in light given by it varied from 30 per cent with a pressure of 0·46 of an inch to over 200 per cent with a small burner and a pressure of 0·84; but although this was an important factor a still more important one remained, and that this was so is shown by the fact that after using for a considerable time the perfecter lost its power to a very great extent, which would not have been the case had its action been purely mechanical.

Platinum is a metal which possesses the property of condensing gases upon its surface and rendering them chemically more active than when in their normal condition; so that if the condensed gases have a tendency to enter into chemical combination, the presence of the metal, especially when heated to a certain extent, will set up chemical action. That this is the case is clearly shown by heating a piece of platinum foil to redness, allowing it to cool until it ceases to be visibly hot, and then holding it in a current of mixed coal-gas and air, when the metal at once becomes red-hot and often reaches a temperature at which the gas is ignited. This is due to its compressing the oxygen of the air and the hydrogen of the coal-gas upon its surface and bringing about their combination,—an action which evolves great heat and raises the platinum to incandescence, although the actual temperature necessary to ignite the gas may not be reached, as the heat required to do this is very great.

In the perfecter the strip of metal, besides regulating the force with which the two streams of gas impinged upon each other, was raised by this action to incandescence in a portion of the flame which otherwise would have been several hundred degrees cooler, and thus converted the hydrocarbons into acetylene, and by its super-heating action reduced the size of the non-luminous zone. After a time, however, the platinum became attacked by the hydrocarbons of the gas, and the carbide of platinum formed ceased to have this regenerating action, and the perfecter lost its potency.

It was this deteriorating action of the coal-gas on platinum which I believe seriously militated against the success of the Lewis incandescent lamp, which was undoubtedly the most promising of its class, but which soon lost its power for this reason.

By placing a platinum wire in the non-luminous zone of a flat flame we can, if care is taken not to distort the flame, draw down the luminous zone to a considerable extent, and if a fine platinum gauze screen be placed on each side of the lower portion of the non-luminous zone it acts in the same way as regeneration does, and gives a considerable increase in luminous surface.

Another way in which the non-luminous and non-effective portion of the flame may be reduced is by increasing the rate of combustion at the bottom of the flame.

Ten years ago Sir James Douglass introduced his multiple Argand, in which a number of circular flames burnt one within the other, whilst a series of deflectors caused a sharp current of air to impinge upon the outer flames at their base, causing a very great increase in the illuminating effect produced per cubic foot of gas consumed. In this burner the outer layers of flame were sacrificed to create an intensity of temperature which should perfect the light-giving power of the interior layers, and by setting up this intense combustion at the base of the flame the service of the burner was raised to 6 candles per cubic foot of 16 candle gas.

A still better example—because more widely known—of the same thing is to be found in Mr. Sugg's London Argand, in which the metal cone round the burner plays the same part as the deflectors in the Douglass burner, although to a smaller extent, whilst the cluster burners also benefit to a certain extent by the increase of temperature that their arrangement brings about, and I cannot help thinking that if our burner makers will attack the question of improving the flat flame by thickening the flame a little and introducing a suitable form of deflector to bring a current of air against the base of the flame, we

*Annual Cost of Maintaining a Light of 48-Candle Power,—say 2000 Hours' Burning.
Results of Tests under Practical Conditions.*

GAS	"Argand"	3	16-candle Lamps consuming each 5 ft. of gas per hour.	30,000 c. ft. of gas at 3/- per 1000 90/- } 93/-
				Renewals of chimneys 3/- }
		1	Small Lamp consuming 6 ft. per hour.	12,000 c. ft. of gas 36/- } 41/-
				Repair of Lamp, &c. 5/- }
"	"Regenerative burner."	2	No. 2 "Bray" Burners consuming each 3½ ft. per hour, carburetted with naphthalene.	14,000 c. ft. of gas 42/- } 55/-
				52 lbs. of naphthalene at 3d. 13/- }
		1	New Large Mantle, 48-candle power, burning 3½ ft. per hour.	7,000 c. ft. of gas 21/- } 30/-
				Renewal of mantles, 3 at 2/6 7/6 } chimneys 1/6 }
PETROLEUM.	Large Lamp.	1	48-candle Lamp burning 1 gallon in 28 hours.	Oil consumed at 7d. per gal. 41/8 } 44/-
				Chimneys, wicks, &c. 2/4 }
		4	12-candle Lamps each burning 1 gallon in 84 hours.	Oil consumed 55/6 } 58/-
				Chimney, wicks, &c. 2/6 }
ELECTRIC. . .	Incandescent.	3	16-candle Lamps absorbing each 56 "Watts."	Cost of Current at 8d., per Board of Trade unit (1000 Watt-hours) .. 224/- } 245/-
				Lamp Renewals, 6 at 3/6 .. 21/- }

shall soon be able to squeeze a couple of candles more service out of these trusty old servants and add an iota more cheerfulness to our gas-lit cities.

The question of how far it may be possible to go in the extraction of light from gas is a question so complex that I hesitate to even mention it this morning, but I think that many things point to the best forms of regenerative burner, having nearly reached the limits of practical possibilities, so that in conclusion it may be well to see in what other direction the development of light from coal-gas may yet extend.

The 4 per cent or thereabouts of heavy hydrocarbons, which in the ordinary combustion of coal-gas yield the acetylene necessary for the liberation of the carbon particles which are essential for the production of luminosity, are so small in quantity as compared with the constituents which in the burning of flame merely generate heat, that the idea naturally arose of the incandescent burner, in which by admixture of air with the coal-gas before combustion, a non-luminous but hotter flame could be produced and utilised for heating various refractory materials up to incandescence, so that they, and not the carbon, should emit the light.

In burning coal-gas from an open tube the highest temperature attained is about 1100° C. = 2012° F., whilst in the more perfect combustion taking place in a flat flame 1368° C. = 2462° F. is attained; but by mixing air with the gas before combustion as in the ordinary Bunsen burner until the mixture burns with a quiet and non-luminous flame, a temperature of 1500° C. = 2732° F. is reached, whilst by increasing the quantity of air until the flame is on the point of flashing down in the tube, the temperature rises to 1630° C. = 2966° F., or nearly 300° C. hotter than the luminous flat flame, and it is this high temperature which is taken advantage of to raise the various materials used in incandescent burners to the point at which they emit the required light.

In order to gain a relative idea of the service obtained per 5 cubic feet of 16 candle gas from the various classes of burner, choosing the best of each kind for comparison, we may take it as being as follows:—

Service yielded by Various Burners per Five cubic feet of Gas an Hour.

Flat flame.	12.5
Argand ordinary	14.0
London Argand	16.0
Regenerative	52.5
Incandescent	70.0

A colleague of mine at the Royal Naval College, Prof. Lambert, has been for some time past experimenting in

his own house as to the cost of various forms of illumination on a domestic scale, and his results for actual working over a considerable period he has kindly placed at my disposal.

The only remark I have to add to this extremely interesting and useful table is that Prof. Lambert has been extremely fortunate with his incandescent mantles and chimneys, whilst the regenerative lamp employed is manifestly too small to give anything approaching its maximum results. My own experiments would lead me to say that the incandescent and regenerative burners, taking everything into consideration, are as nearly as possible equal in cost, each of them yielding the above amount of light for an expenditure of about 35/-.

In the search, moreover, for the best method of generating light from coal-gas, we must not overlook the quality of the light emitted, and we should remember that the yellow light given out in the consumption of coal-gas is eminently adapted for resting the eye wearied by the actinic rays of the daylight, and that although an intense white or bluish white light is admirably adapted for use in picture galleries and other situations where it is necessary to bring out delicate shades of colour, yet that in the living and working room such a light must in time affect the eyesight more or less. Incandescent lighting is still in its infancy, and it has yet to be discovered how to make a mantle or comb which will not deteriorate in use and which shall not be too brittle to withstand the jars of every day use.

I have in this lecture attempted to place before you a general outline of the wonderful growth of our present methods for developing light from coal-gas, and we may be well proud of the results of the work done in the past century; but is there no reverse to this picture? Has everything been done which might have been done to encourage and increase the demands for gas? The gas managers and engineers of this country may have been a little tardy in recognising new principles, but their record is a noble one, and the one error which has been made does not rest upon their shoulders. For coal-gas to take its proper place it must be supplied at the cheapest possible rate, and all statistics show us that the increase in consumption when the price of gas is low is very large indeed, and the one thing which has more than anything else kept back the gas industry has been the fixing of the illuminating value at too high a figure. If a 14-candle standard had been adopted here in London instead of a 16, an almost unbearable burden would have been taken off the gas manager's shoulders, and not one consumer in a thousand would have noticed any difference in the light; indeed, a little trouble on the part of the companies in

advising consumers as to the best forms of burner to use would probably have resulted in an absolute gain, whilst the reduction in price consequent on the doing away with need of enrichment would have given an enormous impetus to the use of gas as a domestic fuel.

ANALYSIS OF CHROMITE.

By E. WALLER and H. T. VULTÉ.

CHROMITE, the mineral source of chromium compounds used in the arts, is essentially a chromate of iron, and is represented by the formula $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. The theoretical composition calculated from this basis is—

FeO , 32 per cent.

Cr_2O_3 , 68 per cent.

The mineral is frequently associated with magnesia, silica, and manganese; the full list of possible constituents of the ore is that usually given for iron ores.

The chromium is usually the most important constituent, and chromic oxide alone is determined. The refractory character of chromite is well known, and many efforts have been made to perfect a scheme of separation and estimation of the chromium which would be at the same time simple and accurate.

The following methods may be recalled:—They are divided in two distinct classes. First, those making use of liquid reagents; second, those in which fusion is used. Of the first class we mention the following:—

1. Boiling with nitric acid and potassium chlorate, Storé, *Proc. Amer. Acad.*, iv, 432; Pierson, *Am. Jour. Sci.* [2], 48, 190; Pawolleck, *Ber.*, xvi., 3008. Baubigny, *Bull. Soc. Chem.*, 1884 [2], xli., 291, finds this method very satisfactory. Many others, however, have found it tedious or unsatisfactory, or both, and such has been our experience.

2. Heating with bromine water in a sealed tube at 130° – 170° C., for several days, E. F. Smith, *Am. Jour. Science* [3], xv., 198. It is obvious that the length of this operation constitutes a very serious objection.

3. Heating for several hours at 200° C. with sulphuric acid (1 part H_2O and 2 parts H_2SO_4 by weight) in a sealed tube, Mitscherlik, *Jour. Prakt. Chem.*, 81, 108, and 83, 455.

Sulphuric acid of specific gravity 1.34 was found by Philips, *Fres. Zeits.*, xii., 189, to give the best results. The time required for this operation is about ten hours. Serious objections may be urged against these methods, both from length of time required and danger of explosion. Of the second class, or fusion methods, we find:—

1. Acid potassium fluoride, Gibbs, *Fres. Zeits.*, iii., 328, also Dubois, *Fres. Zeits.*, iii., 401; these chemists use four to five times the weight of ore in flux, and fuse from ten to fifteen minutes.

2. Alkaline or alkaline earth fluoride in conjunction with alkaline bisulphate, Sill, *Jour. Lond. Chem. Soc.*, xxxv., 292; Clarke, *Am. Jour. Science*, 1868, 173; Hagen, *Untersuchungen*, i., 163. The use of fluorides require special management to avoid the subsequent destruction of glass-ware, and involves more manipulation and skill than is required by some of the other methods.

3. Potassium bisulphate alone, Reinhardt, *Chem. Zeit.*, xiii., 430. This method is not efficient unless extraordinary precautions are taken in pulverising the ore.

4. Potassium bisulphate followed by potassium chlorate and sodium carbonate, O'Neill, *CHEM. NEWS*, 1862, 199.

5. Potassium bisulphate followed by potassium nitrate and sodium carbonate, Oudeslays, *CHEM. NEWS*, 1862, 254. Hunt, *Amer. Jour. Sci.* [2], v., 418, adds a little alkaline nitrate towards the end of the operation.

6. Caustic alkali with or without the addition of lime, Pellet, *Berg. u. Huttenman Ztg.*, xl., 224; Christomanos, *Ber.*, x., 10, substitutes magnesia for lime. Morse and Day, *Amer. Chem. Jour.*, iii., 163, advocate the use of an iron crucible.

7. Caustic or carbonated alkali in conjunction with an oxidising agent. Potassium chlorate is recommended by Schwartz, *Annalen*, lxxix., 212, and Blodgett-Britton, *CHEM. NEWS*, xxi., 266. Alkaline nitrate is recommended by Calvert, *Jour. Lond. Chem. Soc.*, v., 194; Peligot, *Comptes Rendus*, 67, 871; Clouet, *Comptes Rendus*, 67, 762. Barium dioxide is recommended by Donath, *Ding. Polyt. Jour.*, cclxiii., 245; Kinnicut and Paterson, *Jour. Anal. Chem.*, iii., 132.

8. Alkaline carbonates with borax, Dittmar, *Ding. Polyt. Jour.*, ccxli., 450, and iron, January, 1876, p. 131. The flux is composed of three parts of a mixture of potassium and sodium carbonates with two parts of borax glass.

9. Alkaline carbonate with some borax and alkaline nitrate, P. Hart, *Jour. Prakt. Chem.*, lxxvii., 320.

The wet methods and those by fusion with fluoride have already been briefly discussed. Fusing alkaline bisulphate, in our experience, does not readily decompose chromite unless it is in a state of subdivision not easily obtained. Elutriation is not a desirable method of obtaining the necessary state of comminution, since the chromite possesses such a high specific gravity (about 4.5) that by elutriation a partial separation of that mineral from its associated minerals in any given sample will result, tending to produce incorrect results.

Fusion with caustic alkalis requires the use of a silver or iron crucible. Such crucibles need to be thick as compared with those of platinum, and consequently require the application of a higher heat to keep the melt at the proper temperature during fusion. Moreover, if oxidising agents are used in these crucibles they deteriorate rapidly.

Of course, where alkaline fluxes only are used, the decomposition is effected by the oxidation of the chromium to chromic acid and its union with the alkali. The presence of an excess of base, with a plentiful access of the oxygen of the air, favours such a change, and indeed is the method utilised in the manufacture of chromium salts from the ore.

The following process based on such a fusion with subsequent special treatment has been found to give satisfaction, and is thought to be more simple, accurate, and rapid than any method heretofore proposed. The plan of procedure is:—

a. Fuse 0.5 to 1 grm. with five or six times its weight of Dittmar's flux in a platinum dish.

b. Dissolve in water, filter, and evaporate, adding a little ammonium nitrate from time to time, until the last addition fails to give any odour of ammonia on heating the solution. Continue the evaporation to dryness, moisten with a few drops of nitric acid, and heat until dry.

c. Take up with water containing a few drops of nitric acid, add hydrochloric acid and sulphuric acid, or a little ammonium sulphite, boiling out the excess of SO_2 .

d. Neutralise with ammonia and boil, adding a little ammonium sulphide. Re-dissolve in hydrochloric acid, and re-precipitate as before to purify the precipitate. Ignite and weigh Cr_2O_3 .

Comments.—a. The flux is made by fusing together two parts of borax glass with three parts of (dry) sodium and potassium carbonates, mixed approximately in proportion of their molecular weights (106 to 138). After fusing the mixture is poured out upon a cold surface (a dry platinum dish floated on the surface of cold water), and then coarsely powdered for use. As it is somewhat hygroscopic, it should be kept in a tightly corked bottle. The borax makes the flux somewhat pasty, so that it holds the mineral partly in suspension, and thus favours the decomposition. A convenient form of dish for the fusion is one about 2 inches in diameter, and half an inch deep, with rounded bottom, and provided with a small ear for grasping with the tongs. If a shallow dish of the kind is not available, the convexity of the cover of a large fusion crucible makes a very good substitute. The flux has

practically no effect upon the platinum. Over three hours of fusion caused in one case a loss of 3.5 m.grms. and ordinarily little or nothing.

A good way of managing the fusion is first to melt in the dish the requisite quantity of flux, and then allow it to cool; then weigh out the finely pulverised ore, and, by means of a feather, brush it on to the surface of the melt, spreading it as evenly as possible.

Then fuse with a good Bunsen burner, stirring occasionally with a platinum wire, until the decomposition is apparently complete. This is likely to require not over forty minutes, if the ore has been well pulverised and the stirring has been sufficiently frequent. If either point has been neglected it may require longer. Remove the heat temporarily, and, as the mass cools, stir with the platinum wire in such a way as to take a portion of the material from the bottom of the melt. As soon as this hardens sufficiently, withdraw and examine it for black grains of undecomposed ore. If any are seen, replace the test bead in the dish, cover, and apply the heat. The material soon melts off from the wire, when the cover may be removed, unless the heat is insufficient to keep the mass fluid without its use. When decomposition is apparently complete, remove the heat and allow the mass to cool.

b. The portion soluble in water, besides the excess of the constituents of the flux, should contain all of the chromium as alkaline chromate, together with some alkaline manganate, aluminate, and silicate. That insoluble in water should dissolve completely in hot dilute hydrochloric acid. If some black grains of undecomposed ore remain, they must be filtered off and fused with a little more of the flux, as in the first instance.

The evaporation of the water solution, with addition of ammonium nitrate (Genth, CHEM. NEWS, vi., 32), cause the manganese to separate as insoluble MnO_2 , the alumina being at the same time precipitated as hydrate, which, by the prolonged heating, assumes a form practically insoluble in nitric acid, especially when hot. The last addition of nitric acid and heating will render all the silica insoluble, so that eventually nothing soluble remains except alkaline chromate and nitrate.

c. The object of this step is simply to reduce the chromium to the form of base. The presence of hydrochloric acid is of advantage in the next step, as it affords ammonium chloride, which favours the separation of chromium hydrate.

d. It may be found that at first no precipitate appears on neutralising with ammonia. On boiling, however, to remove the slight excess of ammonia, chromium hydrate separates. The addition of a little ammonium sulphide favours the separation. The precipitate produced in presence of the fixed alkalis is, however, never sufficiently pure to be at once ignited and weighed. After washing it requires at least one re-solution in hydrochloric acid and re-precipitation in the same manner as before. A third re-precipitation may be advisable.

If alkaline salts remain with the precipitate, the error involved is not only due to the additional weight of those contaminants, but they may induce a further increase in weight due to the partial formation of alkaline chromate.

List of analyses made by the preceding method:—

	Cr_2O_3 found per cent.	Cr_2O_3 calc. per cent.
1. Chromite and iron ore ..	4.18	4.38
2. " " " ..	2.92	2.80
3. " " " ..	3.87	3.96
4. " " " ..	2.75	2.64
5. " " " ..	2.57	2.72
6. " " " ..	2.98	2.88
7. " " " ..	4.44	4.32
8. " " " ..	4.027	4.07
9. " " " ..	8.44	8.64
10. " " " ..	3.52	3.51
11. " " " ..	2.77	2.907
12. " " " ..	10.57	10.60

These samples were made from a chromite mixed with iron and manganese ores. The chromite was found to contain 57.00 and 57.025 per cent of chromic oxide as a result of determination by different analysts.—*School of Mines Quarterly*, xiii., No. 3.

THE OFFICIAL METHOD FOR THE ANALYSIS OF NON-STARCHY FOODS (COARSE FODDERS, OIL SEEDS, AND OTHER RESIDUES) FOR 1890—91.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION
OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

Preparation of the Sample.

THE substance is to be ground until all of it will pass through a sieve with circular holes 1 m.m. in diameter.

Hygroscopic Water.

Dry 2 to 3 grms. of the substance for four hours, heated fully to the temperature of boiling water, in a current of dry hydrogen, but without allowing the glass containing it to come in contact with the boiling water.

Ash.

Char the substance at a low red heat, which is conveniently done in a Fletcher gas muffle furnace, heated not by the large gas burner that is supplied with the furnace, but by a Fletcher solid flame burner (No. 46b); exhaust this charred mass with water; collect the insoluble residue on a filter, burn, add this ash to the residue from the evaporation of the above aqueous extract, and heat the whole to low redness till the ash is white.

Ether Extract.

Extract 2 to 3 grms of the substance, dried as for the determination of the moisture, with anhydrous and alcohol-free ether, sixteen hours. Dry the extract by exposure to the full heat of boiling water, in a current of dry hydrogen, to constant weight.

Crude Protein.

Determine nitrogen by the Kjeldahl method as directed for nitrogen in fertilisers, and multiply the result by 6.25 for the crude protein.

Albumenoid Nitrogen.

Stutzer's Method.—Prepare cupric hydrate as follows: Dissolve 100 grms. of pure cupric sulphate in 5 litres of water, and add 2.5 c.c. of glycerin; add dilute solution of sodium hydrate until the liquid is alkaline; filter; rub the precipitate up with water containing 5 c.c. of glycerin per litre, and then wash by decantation or filtration until the washings are no longer alkaline. Rub the precipitate up again in a mortar with water containing 10 per cent of glycerin, thus preparing a uniform gelatinous mass that can be measured out with a pipette. Determine the quantity of cupric hydrate per c.c. of this mixture. To 1 gm. of this substance add 100 c.c. of water in a beaker, heat to boiling, or in the case of substances rich in starch heat on the water bath ten minutes, add a quantity of cupric hydrate mixture containing 0.7 to 0.8 gm. of the hydrate, stir thoroughly, filter when cold, wash with cold water, and put the filter and its contents into the concentrated sulphuric acid for the determination of nitrogen after Kjeldahl. For the above filtration use Schleicher and Schüll's No. 589 paper, or Swedish paper, either of which contains so little nitrogen that it can be left out of account.

If the substance examined consists of seed of any kind, or residues of seeds, such as oil cake or anything else rich in alkaline phosphate, add a few c.c. of a concentrated solution of alum just before adding the cupric

hydrate, and mix well by stirring. This serves to decompose the alkaline phosphate. If this is not done cupric phosphate and free alkali may be formed and the protein copper may be partially dissolved in the alkaline liquid.

Crude Fibre.

Extract 2 grms. of the substance with ordinary ether, at least nearly completely, or take the residue from the determination of the ether extract. To this residue, in a 500 c.c. (Erlenmeyer) flask, add 200 c.c. of boiling 1·25 per cent sulphuric acid; connect the flask with a return-flow condenser, the tube of which passes only a short distance beyond the rubber stopper into the flask. Boil at once, and continue the boiling for thirty minutes. A blast of air conducted into the flask may serve to reduce the frothing of the liquid.

Filter, wash thoroughly with boiling water till the washings are no longer acid, rinse the substance back into the same flask with 200 c.c. of a boiling 1·25 per cent solution of sodium hydrate at least almost free from sodium carbonate, boil at once, and continue the boiling for thirty minutes in the same manner as directed above for the treatment with acid. Filter in a Gooch crucible and wash with boiling water till the washings are neutral, dry at 110° C., weigh, incinerate completely, and give the loss of weight for crude fibre.

The filter used for the first filtration may be linen, one of the forms of glass wool, and asbestos filters recommended in the last report, or any other form that secures clear and reasonably rapid filtration. The carbonate free sodium hydrate can be obtained of the Troy Laundry Machinery Company, 32, Dey Street, New York, or 297, Wabash Avenue, Chicago, under the name of "Greenbank Alkali Company," double refined 98 per cent caustic soda, it being the same as that recommended for the Kjeldahl nitrogen method. The solutions of sulphuric acid and sodium hydrate are to be made up of the specified strength accurately by titration, and not merely by the areometer.

**AN IMPROVED METHOD OF DETERMINING
SMALL PERCENTAGES OF SILVER AND GOLD
IN BASE METALS, MATTES, &c.***

By CALLEB WHITEHEAD,
Assayer to the Mint Bureau, Washington, D.C.

ANYONE having frequent occasion to report the values of silver and gold in such material as crude copper, copper mattes or ores, metallic iron, zinc, &c., will appreciate the advantages of a method which affords accurate results with little expenditure of time. The large production of pure copper by electrolytic methods from silver- and gold-bearing copper ores, renders some such method very desirable in view of the various transfers of,—(1), ores to the smelters; (2), mattes to the refiners; and last, the crude copper to the electrolytic refinery; each of which transfers carries a commercial charge of the bullion contents.

While the proposed method is available for a great variety of base products, it will perhaps be best illustrated by its use in determining the silver and gold contents in crude copper, or the mattes resulting from bullion-bearing copper ores. The adaptability of the method to other base metals will readily suggest itself to the experienced assayer.

Given a crude copper or matte carrying from 30 ounces of silver and 0·10 of an ounce of gold, upward, the usual method would be scorification. It is usual to take for assay from 0·05 to 0·1 assay ton to each scorifier, with which are used from 40 to 50 grms. of test-lead, one-half of which is mixed with the ore in the scorifier and the remainder used as a cover. The scorifier is now intro-

duced into a hot muffle and the door closed until the lead is melted, when it is opened, and about 1 grm. of borax glass placed on the lead. Oxidation begins at once, and the lead and base metals are rapidly scorified off until the slag covers the metal, when the assay is poured into a mould. If the lead button still retains much copper, or is hard or brittle, it is again scorified, with the addition of more test-lead if necessary. When the lead button is soft and of proper size, it is cupelled and the button weighed and parted. Several scorifications are sometimes necessary before the button is ready for the cupel.

The two objections to this method are, first, the loss of silver during scorification and cupellation, the latter due chiefly to the copper remaining in the lead, which it is practically impossible to remove in the scorifier, and which takes silver into the cupel. These losses I found to amount to from 2·33 to 2·78 per cent of the silver present in the copper. My experiments were made with pure copper and pure silver, the silver being added in the proportion of 100 ounces per ton of alloy.

The second objection is the small amount of bullion which can be operated upon, which necessitates the use of many scorifiers where small amounts of gold are to be estimated, which is usually the case.

To avoid the doubtful results of scorification processes the following method has been adopted at the copper works of a firm having large interests at stake:—

One assay ton of copper is dissolved in nitric acid, diluted, and allowed 24 hours to settle. The solution is now filtered from the slight sediment containing the gold. A few drops of hydrochloric acid are added to the filtrate and the solution again allowed 24 hours for silver chloride to deposit, when it is filtered, washed, and the two filters dried, combined, scorified with test-lead, and cupelled. The chief objections to this are—(1), the time required; (2), the small amount of precipitate obtained and the danger of loss in scorifying silver chloride; (3), the greater solubility of silver chloride as compared with the bromide.

While the method used at these works is an advance over previous practice, yet the time employed and the uncertainties indicated leave much to be desired. The protracted time allowed for settling is necessitated by the exceedingly fine condition of the gold resulting from the solution of a metal carrying possibly from 0·10 to 5 ounces of gold per ton of metal. It would pass through a filter unless allowed to aggregate by standing.

The larger quantity (say 100 ounces) of silver per ton will give but a slowly subsiding cloud (impossible to filter) when newly precipitated as chloride. The scorification of these combined precipitates, one of them being silver chloride, cannot give results quite satisfactory, despite the time involved, some 48 hours at least.

The method which I will now briefly describe was devised to meet just such cases, and is suitable for the bullion valuation of zinc, iron, nickel, &c., as well as the sulphides and arsenides of iron and copper. To illustrate the proposed method, which has been found effective and useful, the treatment is detailed for a crude metallic copper carrying both silver and gold. It will be understood that sodium bromide is chosen as a precipitant because of the greater insolubility of silver bromide over the chloride, and also that the soluble lead salt is added in order that the heavy precipitate of lead bromide may envelop and promptly carry down the silver bromide cloud, which otherwise would require long waiting for its subsidence, as well as to furnish the lead necessary for cupellation.

Weigh out from one to four a. t., depending upon its richness, place it in a beaker of 500 c.c. capacity, and add gradually enough nitric acid to dissolve it completely, heat until red fumes cease to come off, dilute with water, and add 50 grms. of lead acetate, stir, and when dissolved add 1 c.c. dilute sulphuric acid, and allow the lead sulphate to settle. Filter into a 1000 c.c. flask, and fill to the mark with distilled water.

* Read at the Chemical Section of the Franklin Institute, May 17th, 1892.

The filter contains the gold which has been collected and carried down by the sulphate of lead. The filter-paper and precipitate are dried, the paper burned, and the ash and lead sulphate scorified with test-lead. The button is cupelled and the gold, with any trace of silver it may contain, is weighed. Add silver and part the gold in the usual way. Note the amount, if any, of silver found, and include the proper proportion of the amount with that found in the solutions as about to be described.

In order that there may be a control assay, the solution is divided into two equal parts, to each of which a saturated solution of sodium bromide is added with constant stirring as long as a precipitate is produced. The precipitates settle quickly and filter and wash well. Cold water only should be used, and the washing be continued until the washings are free from copper. Any bromide of lead dissolved during the washing may be neglected, as I have never found it to contain more than a trace of silver, even when assaying ores carrying many thousand ounces.

The precipitate when dry can be brushed from the paper without difficulty, and thus the trouble of burning the filter is avoided. The bromides are now mixed with three times their weight of carbonate of soda and a small amount of flour or other reducing agent placed in a small crucible covered with borax glass and melted down in the muffle. The button should weigh about 2 grms. and be free from copper and other injurious impurities. This button is cupelled at a low temperature, so that the cupel "feathers" nicely. The time required is from three to five minutes. Duplicate assays usually agree within two-tenths of an ounce per ton.

The following examples are from copper bullion:—

	Silver Ounces.	Ounces.	Gold. Ounces.
No. 1	61'30	61'20	0'10
No. 2	63'45	63'30	0'17

Had the gold button contained silver, one-half of its silver contents would have been added to the silver recovered from the solutions, since the gold is estimated on the whole weight, while two determinations of silver are made on the same weight.

The following is an example from a silver-bearing cast iron from the U.S. Mint at Philadelphia. It was dissolved in nitric acid, diluted, and precipitated with lead and sodium bromide. After washing, the bromides were dried and brushed from the filter. No. 1 was mixed with 10 grms. of litharge, a little flour, the usual amount of soda, and covered with borax. Melted down and cupelled the button gave 30'80 ounces per ton. No. 2 was mixed with test lead and borax, and scorified. It gave 20'90 ounces per ton, 0'90 of an ounce less than No. 1. However, this would be considered a very close agreement by the old method.

The following is an ore from Colorado, very base and with a gangue of sulphate of barium. It proved very unsatisfactory to assay by scorification, duplicates not agreeing at all. The ore was treated with nitric acid and filtered, the residue being assayed separately.

The following are my results:—

	No. 1. Ounces.	No. 2. Ounces.
Residues	32'50	35'95
Solutions	454'90	453'30
As a total	487'40	489'25
Difference of	1'80	—

Gold was not separated in the residues. The highest assay gotten by scorification was about 467 ounces, which shows 20 ounces in favour of the new method, with a reasonably close agreement in different assays.

Pipettes for Hydrofluoric Acid.—G. P. Vannier (*Journal of Analytical Chemistry*).—These instruments are constructed of ceresine, which is not attacked by hydrofluoric acid.

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 9.)

II.—SYNTHESIS OF CUPRIC SULPHATE.

PARALLEL with the experiments which have just been described was commenced a series of syntheses of cupric sulphate. It was hoped that the results might furnish a valuable confirmation to the conclusions based upon the analytical work, but the outcome of the series was very disappointing.

The method of experiment was as follows:—A weighed amount of pure electrolytic copper (for mode of preparation, see *Proc. Amer. Acad. Arts Sci.*, xxv., 199, 206), which had been ignited in hydrogen, was dissolved in the purest nitric acid in a platinum flask provided with bulb tubes for the condensation of spray. A slight excess of pure sulphuric acid was then added, and the whole was evaporated to small bulk in a platinum dish. After transferring to a small crucible enclosed in a larger one, the remaining solution was evaporated to dryness on the steam bath; and the residue was gradually raised to a temperature of 400°. After some time the crucible was quickly covered, placed in a phosphoric oxide desiccator, and allowed to cool in a vacuum. Air having been admitted through suitable drying tubes, the crucible was quickly weighed. The product of the experiment soon reached constant weight upon re-heating, but it was invariably found to contain a very perceptible amount of imprisoned sulphuric acid, which rendered its solution strongly acid to methyl orange. It is evident from the preceding section that this impurity is not retained when pure sulphuric acid is added to powdered cupric sulphate which has already been nearly dehydrated, but only when the salt is crystallised from strongly acid solutions. This fact rendered the present experiments useless for their original purpose. The results of the two determinations show how insidious constant error may be, if not guarded against by check experiments.

Synthesis of Cupric Sulphate from Metallic Copper.

(Weights reduced to vacuum. Sp. gr. of Cu = 8'95; of CuSO₄ (Hampe and Karsten) = 3'61).

No. of experiment.	Metallic copper taken. Grms.	Cupric sulphate found. Grms.	Per cent of copper in cupric sulphate.
40.	0'67720	1'7021	39'786
41.	1'00613	2'5292	39'781

Average 39'784

From analysis of cupric sulphate dried at 400° 39'807

In order to show that the large difference between these two averages was due solely to the occlusion of sulphuric acid, the following experiment (No. 42) was made:—3'1227 grms. (in vacuum) of the purest crystallised cupric sulphate were dried at 400°, the residue weighing 1'9963 grms. The nearly anhydrous salt was then carefully dissolved in water, and after the addition of small quantities of nitric and sulphuric acids it was evaporated and ignited at a temperature even somewhat higher than before. A gain of 0'0013 gm. was apparent, very nearly corresponding to the difference noted above. The acids, tested immediately afterwards, left no weighable residue upon evaporation.

While it was apparent that these experiments were useless for their original purpose, it was hoped that their comparison with similar syntheses from cupric oxide might furnish valuable indirect evidence with regard to

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

the quantitative relations of the latter important substance. The hope was not in vain.

The cupric oxide used as the basis of the three following experiments was prepared essentially in the manner described in *Proc. Amer. Acad. Arts Sci.*, xxv., p. 199. The three experiments represent as many different preparations, in making which various different precautions were observed; but in a paper already far too prolix the omission of these minor points will be well pardoned. The cupric oxide was ignited to constant weight at a dull red heat in a double crucible, and cooled in a vacuum as usual. The outside crucible was of platinum in the second and third experiments, and in these cases the inner crucible was observed to have gained noticeably in weight during the ignition. The last weight was adopted, for obvious reasons. In the first and last cases the solution of the oxide was conducted in the crucible, without transferring, while in the second experiment the cupric oxide was dissolved in the platinum flask with bulb tubes. In each case both nitric and sulphuric acids were added, that the conditions might be similar to those of the preceding syntheses. The cupric sulphate used by Baubigny in his analyses was prepared in a somewhat similar way, and hence in this respect his result is comparable with these.

Synthesis of Cupric Sulphate from Cupric Oxide.

Weights reduced to vacuum. Sp. gr. of CuO = 6.3; of CuSO₄ = 3.61.

No. of experiment.	Cupric oxide taken. Grms.	Cupric sulphate found. Grms.	Per cent cupric oxide in cupric sulphate.
43.	1.0084	2.0235	49.835
44.	2.7292	5.4770	49.830
45.	1.0144	2.0350	49.848
Average			49.838
Theory if Cu = 63.6			49.856
" " = 63.34			49.774
Baubigny's result			49.815

The comparatively close agreement between the average and the theory is solely due to an elimination of opposite errors. This fact will be more evident in the following section.

In order to show that no material was mechanically lost during the syntheses, the last sample of cupric sulphate from each of the two series was electrolysed. The result of one of these electrolyses has already been given in Experiment 16; the other yielded 0.8066 grm. of metal from 2.0350 grms. of the sulphate, or 39.78 per cent of copper.

It is evident that impure cupric sulphate prepared in this manner contains about 39.784 per cent of copper and about 49.838 per cent of ordinary cupric oxide. That is to say, 39.784 parts of copper correspond to 10.054 parts of the remainder of cupric oxide. Assuming this remainder to consist solely of oxygen, the atomic weight of copper would be 63.312. But upon comparing the quantity 10.054 with the quantity of sulphuric anhydride found by difference, 50.162, it is evident that a grave error exists in the former figure. This error becomes only more apparent when allowance is made for the occluded acid.

These inferences are based upon data of somewhat uncertain accuracy, it is true; but the error is nevertheless so large as to be apparent even to cruder analysis than this. The full explanation of the results, as well as of the variation exhibited by Baubigny's analysis, must be deferred to the next section. The doubts raised by the data under discussion formed a useful introduction to the study of cupric oxide.

(To be continued.)

Prevention of Bumping in Boiling.—E. Pieszczyk (*Chemiker Zeitung*).—The author suspends in the liquid to be boiled a glass tube, closed above, 5—8 c.m. long and 5—10 c.m. in width.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, June 24th, 1892.

Prof. A. W. RÜCKER, F.R.S., in the Chair.

THE following communications were made "*On Breath Figures*," by Mr. W. B. CROFT.

After mentioning the observations of early experimenters on the subject, the author described a method which he found to give the best result. A coin is placed on a glass plate for insulation. Another glass plate which is to receive the impression is well polished and laid on the coin, whilst a second coin is placed above the first. The coins are put in connection with the poles of an electrical machine, giving one inch sparks for two minutes. When the coins are removed and the glass breathed on, clear frosted pictures of the coins are seen on the glass. The microscope shows that moisture is deposited on the whole surface, the size of the minute water granulation increasing, as the part of the picture is darker in shade. The thickness of the glass seemed to make no difference to the result, and several plates and coins might be piled up alternately. If carefully protected time appears to have little effect on the figures, but they can be removed by rubbing whilst the glass is moist. Failures and their causes were discussed, and the more complex phenomena produced by strong discharges described. It was also pointed out that breath figures could be produced by laying a coin on a freshly split surface of mica, and that a coin laid on glass for some time leaves its traces. Perfect reproductions of printed matter have been obtained by placing a paper printed on one side only between two sheets of glass for ten hours. Some substances such as silk, in contact with glass, give white figures, whilst wool, cotton, &c., give black ones. Various analogous effects are noticed in the paper, and the several views put forward in explanation of the phenomena examined.

A communication on the same subject from the Rev. F. J. SMITH, was read by Prof. Perry. He had investigated some of the effects, and had succeeded in photographing the impressions, prints from which were shown. He had also examined the influence of various gases on the result, and found that oxygen gave the best figures. In a vacuum no figures could be obtained. The effect of temperature had also been tested.

Prof. S. P. THOMPSON said details of early researches were given in *Poggendorff's Annalen* for 1842. It was there pointed out that better results were obtained by putting a spark gap between the coin and the machine. Since the effects did not depend on the way in which the sparks passed, he thought it was probable that electrical oscillations were involved. He himself had worked at the subject in 1881, and recently repeated some of the experiments. Figures could be produced on almost any polished surface. He got best results by using a small induction coil giving about 3 m.m. spark for about five seconds. In 1881 he accidentally noticed that photographs could be got on ebonite. Hot coins put on uncleaned glass gave good breath figures.

A MEMBER said that instead of breathing on the plates he and Mr. Garrett had sifted finely powdered red lead over them to get the figures. They had also fixed the figures by etching with hydrofluoric acid.

Mr. CROFT exhibited some figures he obtained two years ago which were still quite distinct.

"On the Measurement of the Internal Resistance of Cells," by Mr. E. WYTHS SMITH.

After referring to the methods hitherto used, the author explained a modification of Mance's test which he had recently devised. One pole of the battery to be tested is connected to the similar poles of two other batteries. Each battery has a separate circuit, through which

currents are allowed to pass. Selecting a point A at the opposite pole of the battery to be tested, points B and C in the circuits of the auxiliary batteries are found whose potentials are equal to that of A. The resistances between each pair of points, AB, AC, BC, are then measured by a Wheatstone bridge. Calling these resistances R_1 , R_2 , and R_3 respectively, it is shown that the internal resistance required is given by the formula—

$$b = x + \frac{x^2}{r} + \frac{x^2}{r^2} + \&c., \text{ where } x = \frac{R_1 + R_2 - R_3}{2},$$

and r is the external resistance of the circuit containing the battery tested. For an accumulator discharging $b = x$ to within about 2 per cent.

Prof. PERRY inquired how far the results obtained agreed with those got by the older methods, and whether they depended on the time the keys were kept down. In the old methods it was assumed that an instantaneous rise in P.D. occurred on breaking the circuit. This might or might not be true. He was inclined to regard the P.D. and current as functions both of resistance and time. The behaviour of cells seemed to indicate the existence of something like capacity, or rather, capacities and resistances in series.

Prof. AYRTON said the paper was of great interest, for it made possible what could not be done before, viz., to find the resistance of a cell without appreciably altering the current through it. Although the new method required more cells this was not prohibitive, for the result sought was of considerable scientific importance. The same method was applicable for finding the resistance of dynamo armatures when working, a quantity which had hitherto been unattainable by direct measurement.

Mr. LANE FOX said the perplexing changes in the P.D. of secondary cells were to be accounted for by changes in the electrolyte which occurred in the pores of the plates. He could detect no flaw in the reasoning given in the paper.

Dr. SUMPNER remarked that the method was a valuable one, for it depended on bridge tests, which could be made with considerable accuracy. On the other hand, it was a false zero method, and therefore liable to errors arising from changes of this zero.

Prof. AYRTON pointed out that these errors could be eliminated by reversing the bridge battery.

Mr. RIMINGTON said although the testing currents were small they might affect the E.M.F., and thus introduce an error in b . This could be tested by using alternate currents and a telephone.

In reply to Prof. Perry, Mr. SMITH said the results agreed with those obtained by the older methods to within the limits of accuracy obtainable by the latter methods; this might amount to something like 15 per cent.

"On the Relation of the Dimensions of Physical Quantities to Directions in Space," by Mr. W. WILLIAMS.

In February, 1889, Prof. RÜCKER recalled attention to the fact that in the ordinary dimensional formulæ for electrical quantities the dimensions of μ (permeability) and k (specific inductive capacity) are suppressed. In the discussion on that paper Prof. S. P. THOMPSON pointed out that lengths should be considered as having direction as well as magnitude, for if so regarded, difficulties arising from different units, such as *couple* and *work*, having the same dimensions would be avoided. Developing this idea, the author takes three mutually perpendicular lines, along which lengths are measured. Calling unit lengths along these lines X , Y , and Z respectively, the various dynamical units, such as velocity, acceleration, force, work, &c., are expressed in terms of M , T , X , Y , and Z . The formulæ then denote the directional as well as the numerical relations between the units, and the dimensional formulæ are therefore regarded as the symbolical expressions of the physical nature of the quantities, so far as they depend on lengths, mass, and time. In this system areas and volumes are represented by products of different vector lengths, instead of

by powers of a single length, and angles and angular displacements by quotients of rectangular vectors, instead of being pure numbers. For physical purposes pure numbers may be defined as ratios of concretes of the same kind similarly directed (if directed at all). A plane angle has dimensions $X^{-1}Y$, X being in the direction of the radius, and Y that of the arc, whilst solid angles have dimensions YZX^{-2} and radii of curvature Y^2X^{-1} . It is also shown that π is a concrete quantity of the dimensions either of plane or of solid angle. This is of considerable importance in connection with the radial and circuital fluxes in the electromagnetic field.

In deducing the dimensional formulæ for electrical and magnetic units, the rational and simplified relations given by Mr. Oliver Heaviside in the *Electrician* of October 16 and 30, 1891, are used. Instantaneous axes are taken at any point of an isotropic medium (the ether), such that X coincides with the electrical displacements, Y with that of the magnetic displacement, and Z with the intersection of the two equipotential surfaces at that point.

Starting with the relation μH = energy per unit volume, the formulæ for the various quantities in terms of μ are obtained. These simplify down to those of the ordinary electromagnetic system by putting $\mu = 1$ and suppressing the distinction between X , Y , and Z . Similarly commencing with $k E^2$ = energy per unit volume, formulæ in terms of k are obtained which, when simplified as above, give those of the ordinary electrostatic system. Examples of the consistent way in which the results work out are given in the paper, and the whole subject is discussed in detail both by Cartesian and vectorial methods.

The formulæ in terms of μ and k are used to trace out and examine the various analogies between electromagnetism and dynamics, thereby obtaining a connected dynamical theory of electromagnetism. Inquiry is then made to what dimensions of μ and k in terms of M , T , X , Y , Z , render the interpretation of electrical and magnetic units simple, natural, and intelligible as a whole. The conditions imposed (for reasons stated in the paper) are, firstly, that the dimensions of μ and k satisfy the relation $[\mu k] = Z^2 T^{-2}$; secondly, that the powers of the fundamental units in the dimensional formulæ shall not be higher or lower than those found in the formulæ of the ordinary dynamical quantities; and thirdly, that quantities which are scalar or directed must also be scalar or directed when their dimensions are expressed absolutely. Subject to these conditions it is shown that the possible dimensional values of μ and k are eight in number. Of these only two lead to intelligible results. These are (1) $\mu = M(XYZ)^{-1}$ and $k = M^{-1}XYZ^{-1}T^2$, and (2) $\mu = M^{-1}XYZ^{-1}T^2$ and $k = M(XYZ)^{-1}$. According to (1) μ is the density of the medium, electrical energy is potential, and magnetic energy kinetic. By (2) k is the density of the medium, electrical energy is kinetic, and magnetic energy potential. Full interpretations of the dimensional formulæ of all the electromagnetic quantities as obtained in accordance with the above conditions are given in the paper.

Prof. S. P. THOMPSON said the paper was a very important one, and thought the idea of finding dimensions for μ and k , which would rationalise the ordinary dimensional formula, a great step. The use of vectors was a valuable feature, whilst the employment of X , Y , and Z , instead of L , removed many difficulties connected with dimensional formulæ. Other difficulties might be cleared up by paying attention to the signs of the vector products and quotients, and to the order in which the symbols were written. Another important matter was the use of Mr. Heaviside's "rational units,"—a system which merited serious attention. In conclusion, Prof. THOMPSON expressed a hope that in accordance with the resolution of the Electrical Congress at Frankfort, both permeability and specific inductive capacity should be designated by Greek symbols.

Prof. O. HENRICK expressed his admiration of the way in which the subject had been treated in the paper. He

had long held that clear ideas of physical quantities were best got by vectorial methods. He also congratulated the author on his treatment of plane and solid angles as concrete quantities.

In a communication addressed to the Secretaries, Prof. O. J. LODGE remarked that physicists in England were more or less familiar with the advantages of retaining μ and k in dimensional expressions before Prof. RÜCKER's paper of February, 1889, brought the matter closely home to students. The system of mechanical dimensions suggested for electrical quantities in an appendix to "Modern Views of Electricity" was not put forth as the only one possible, but as one having certain probabilities of truth in its favour.

Prof. RÜCKER said that although Mr. Williams and himself had talked over certain minor points in the paper the main ideas brought forward were quite original, having been fully developed by Mr. Williams before the author mentioned the subject to him (Prof. RÜCKER).

A paper on "Molecular Forces," by Mr. W. SUTHERLAND, communicated by Prof. CAREY FOSTER, was taken as read.

The CHAIRMAN announced that both this paper and that of Mr. Williams would be printed in the *Phil. Mag.* during the long vacation, so that they could be fully discussed early next session.

NOTICES OF BOOKS.

Year-Book of Chemistry. Report on the Most Important Advances in Pure and Applied Chemistry. ("Jahrbuch der Chemie." Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie). Edited by RICH. MEYER. Vol. I., 1891. Frankfurt-on-Maine: Bechhold, 1892.

THE Editor points out in his preface that the increase of specialism renders it from day to day more difficult for the student or expert to remain in touch with the general course of discovery and improvement, even in his own peculiar department, much less in the other spheres of chemical research.

We certainly find in not a few scientific journals periodical sketches of the most important results. But these summaries form no complete whole; they are scattered in the periodical literature of the day, and not without a very serious expenditure of time can any experimentalist venture to say that he has seen everything which has been done in connection with any given subject. The evil increases since original work has begun to appear not only in the so-called "languages of culture," but in Bohemian, Polish, Russian, Roumanian, &c. Hence there arise unedifying disputes as to priority, as well as waste of time and trouble, when one chemist takes up a question which, unknown to him, has already been entered upon and perhaps decided. Thus we may welcome a work like the present, which in every year will summarise all the most important chemical work effected in the preceding season.

The editor has secured the co-operation of Professor Dr. H. Beckurts, of Brunswick, for pharmacy and the chemistry of foods and articles of personal consumption; Prof. Dr. R. Benedikt, of Vienna, for the technology of fatty matters; Prof. Dr. C. A. Bischoff, of Riga, for organic chemistry; Prof. E. F. Dürre, of Aix-la-Chapelle, in metallurgy; Prof. J. M. Eder and E. Valenta, of Vienna, in photography; Prof. C. Häussermann, of Stuttgart, for inorganic chemical technology and explosives; Prof. Dr. G. Krüss, of Munich, for inorganic chemistry; Professors Maercker and Bühring, for agricultural chemistry, the technology of the carbohydrates, and the industries of fermentation; Prof. R. Meyer, of Brunswick, for the chemistry of coal tar and colouring matters; Prof. Dr. W.

Nernst, of Göttingen, in physical chemistry; and Dr. F. Röhm, of Breslau, in physiological chemistry.

There is a good opening for a work entrusted to such hands, and we wish it full success.

Catalogue of Chemical Apparatus and Pure Chemicals sold by Townson and Mercer, 89, Bishopsgate Street Within, London, E.C., Wholesale and Export Dealers in Chemical and Scientific Apparatus and Pure Chemicals.

If we compare this catalogue in its present form with the earlier editions we shall see that the enterprising firm in question have made those additions which recent advance in chemical and physical science require. Thus we find here a duly priced list of the appliances for the cultivation and study of microbia, such as sterilising ovens, cultivating troughs, serum inspirators, sterilisers, digesters, incubators, gas regulators, counting apparatus, &c., of the best and most modern constructions, to suit all the requirements of the bacteriologist.

Spectroscopes of different makes and prices now figure quite prominently among the requisites of the analyst and experimentalist. Lovibond's "tintometer" is mentioned as a valuable apparatus for measuring and recording colours, especially for dyers and tissue printers.

Apparatus for gas analysis is supplied in considerable variety according to the designs of Lunge, Orsat, Muencke, Winkler, Hempel, Staedel, Elliott, and others.

In addition to apparatus required in the chemical laboratory, we find here assortments of the appliances required in the study of pneumatics, heat, light, crystallography, acoustics, electricity in all its branches, mechanics.

There are lists of the sets of apparatus recommended by the Science and Art Department, Prof. Wanklyn's sets of apparatus and reagents for the analysis of water and milk; Dr. Graham's set for the analysis of malt, beer, &c.; blowpipe apparatus; sets for the Oxford and Cambridge local examinations; for the diploma of public health; the pharmaceutical set, &c. There is a full and illustrated notice of the devices of Messrs. Fletcher and Co. for the production and application of heat.

In short, the student, the experimentalist, and the manufacturer will find this catalogue a useful guide to the apparatus which they may require for any purpose.

The Chemical Constitution of some Colonial Fodder Plants and Woods. By CHARLES F. JURITZ, M.A., Fellow of the University of the Cape of Good Hope. Wynberg: Wynberg Times Office, 1892.

THIS little book is a step in a direction which is at once very useful and too much neglected. The University of the Cape of Good Hope has, it appears, offered "Fellowships" to graduates on certain conditions. One of these is that: "The holder shall for a term of years devote himself to the study of a definite branch of literature or of science of direct interest to South Africa, such as the ethnology and languages of the native races, the botany or zoology of South Africa, or the chemistry of South African plants and minerals." The author selected the chemistry of South African woods, fodders, and leguminous plants—a subject of great importance, both scientific and practical, and at the same time hitherto much neglected.

He shows the influence of climate on the albuminous constituents of plants which are relatively more abundant in a warm than in a cold climate. The plants grown in the warmer locality of Oudtshoorn contain more albumen than those grown at Stellenbosch, and the latter, again, are richer in albumen than those grown in Europe. An important consideration in comparing South African plants with those of Europe is that the former always

contain a smaller proportion of water; consequently their valuable constituents are relatively larger in proportion. This point comes into special prominence in the various products used for the food of cattle.

As regards tannin, none of the African woods and barks seem to equal those of Australia, though they exceed those of Europe. The richest, the bark of "beukenhout," contains 15.96 per cent of tannin. By an oversight, the trees are tabulated only by their Caffir or Cape-Dutch names; the botanical names should have been given for identification. Another oversight is that mahogany, acacia, *Abies canadensis*, and *Quercus castanea*, are given as European.

The author's pamphlet is not merely useful in itself, but forms a good example which we hope to see largely followed in the Colonies.

We must take the liberty of mentioning that, in the title of this treatise, "chemical composition" would be a more appropriate expression than "chemical constitution."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 25, June 20, 1892.

Phenomena of the Residual Life of the Muscle separated from the Living Being. Physiological Action of the Muscular Bases.—Arm. Gautier and L. Landi.—The authors have already shown that the effect of the anaërobic life of the muscular tissue is to acidify and peptonise a small proportion of its proteic substances. A part of the myoalbumen is changed into caseine and into various leucomaines. The fats do not vary appreciably. No glucose can be found in preserved meat, and the glycogen has completely disappeared, being, in the opinion of the authors, partially converted into carbonic acid and alcohol, both of which have been demonstrated. Urea is not produced in any proportion in preserved meat and ammonia, and its salts do not appear in quantities of any importance. Meats if preserved from atmospheric microbia are incapable of undergoing spontaneously the ureic or ammoniacal fermentation. Hence the anaërobic fermentations which occur in muscular tissue free from microbia differ profoundly from the bacterian fermentations essentially hydrating and ammoniacal. The gases emitted by 100 grms. of meat kept for six days at 39° were found to be—

CO ₂	27.5 c.c.
N	1.1 "
H	4.7 "

The easy production of hydrobilirubine in the economy as soon as boron sets in; the reduction of indigo-blue and purple in our organs; the property which muscular flesh possesses of transforming by mere contact and in the cold a small but constant quantity of free sulphur into hydrogen sulphide, shows in what a state of instability is a small portion of the hydrogen which enters into the constitution of the immediate principles of muscle and of its protoplasms. The authors proceed to describe the physiological action of the bases extracted from the muscular tissue.

The Influence of Mineral Filters upon Liquids containing Substances of Microbic Origin.—M. Arloing.—Filters made of mineral pastes possess precious qualities for their hygienic applications. But they offer, from an experimental point of view, serious inconveniences, which deceive us concerning the true properties

of microbic secretions, and which render it difficult to compare experiments made at different times and places with filtered cultures.

Action of Nitric Oxide upon the Metallic Oxides.—MM. Paul Sabatier and J. B. Senderens.—In a former communication the authors have shown the action of nitric oxide upon metals and upon the lower oxides capable of being peroxidised. These results, completely different from those produced by oxygen, or by the air, show that nitric oxide has a peculiar oxidising power. The study of its action upon the peroxides shows that it may also act as a reducing agent. The reduction of chromic acid begins at the ordinary temperature. Silver oxide is not resolved into its elements if heated below 200°, but nitric oxide easily reduces it at 170° and upwards. Lead peroxide, PbO₂, if heated alone is perfectly stable below 450°. Its decomposition takes place only at a red heat, and it then yields orange minium, which, on prolonged ignition, is converted into yellow litharge. In nitric oxide the reduction commences about 315° and proceeds regularly at this temperature, yielding at once white litharge, perfectly homogeneous. Manganese dioxide, which evolves oxygen only at a red heat, acts upon nitric oxide at 400° and is converted into brown sesquioxide. Nitric oxide may be utilised in the production of nitriles. The oxide to be experimented upon was suspended at first in de-aërated water by means of washers traversed at first by a current of hydrogen. Nitric oxide absolutely free from nitrous vapour is then directed upon it, when there is an exclusive formation of nitriles.

On a Phosphorus Bromonitride.—A. Besson.—The compound PBr₂N appears after sublimation as colourless, highly refringent crystals of a rhomboidal form. It melts at 188° to 190°, and begins to sublime at 150° in a vacuum. It is insoluble in water, soluble in ether, but less soluble in carbon sulphide and chloroform.

On Permolymbdic Acid.—E. Péchard.—Crystalline permolybdic acid has a composition expressed by the formula Mo₂O₇ + 5H₂O. At 100° it loses 4 mols. water; the last mol. of water and the oxygen are expelled only at higher temperatures. Permolymbdic acid may be regarded as monobasic. The yellow colouration which oxygenated water gives with alkaline molybdates is due to permolybdates, and turns to orange on the addition of an acid. This reaction has been employed by Denigès to detect traces of hydrogen peroxide.

The Changes of Chalybeate Mineral Waters when Preserved.—J. Riban.—The author shows that the majority of reputed ferruginous waters, as bottled for consumption lose the whole or the larger part of their iron, which is precipitated, and the small quantity which remains in solution is in the ferric state.

The Conversion of Gallic Acid into Pyrogallol. Melting-Point of Pyrogallol.—P. Cazeneuve.—On adding to gallic acid double its weight of aniline, the mixture congeals abruptly into a mass, with a rise of temperature. On the application of heat aniline pyrogallate is obtained in long, instable crystals, from which the aniline may be removed by cold benzene and toluene, leaving pure pyrogallol. The melting-point of pyrogallol is 132° (not corrected), and not 115° as stated by the text-books.

Zeitschrift für Analytische Chemie.
Vol. xxxi., Part 2.

Explanations as to the Wine-Statistics of Germany.—This voluminous memoir, even if space would permit its insertion, could have little interest for our readers.

Quantitative Determination of Uric Acid.—H. Ch. Geelmuyden.—The author describes a number of interesting experiments, but considers it not as yet advisable to

propose a new method on the basis of the results obtained.

Determination of Chlorine in Wine.—W. Seifert.—The author neutralises the wine with sodium carbonate, evaporates to dryness in the usual manner, incinerates and dissolves the ash in dilute nitric acid free from nitrous acid, avoiding large excess, and then proceeding exactly according to Volhard's method.

Apparatus for Determining Carbonic Acid with an Automatic Afflux of Acid.—Greiner and Friedrichs.—This apparatus cannot be described intelligibly without the two accompanying figures.

Weighing Precipitates upon Dried Filters.—Fr. Rüdorff (*Zeit. für Angew. Chemie*).—The author uses a filter extracted with hydrochloric and hydrofluoric acids. He places such a filter in a small cylindrical glass with a cap ground to fit. He uses glasses of 75 m.m. in height and 34 m.m. in diameter. The glass with the filter is placed in a drying closet previously heated to the required temperature, the cap of the glass having been laid upon the closet. After the lapse of thirty minutes the glass is taken out and the cap is immediately applied. The closed glass is then allowed to cool without the use of the exsiccator for thirty minutes, the last ten of which are passed in the balance case; it is then weighed. The precipitate is then filtered off, and washed and dried at 100° on the funnel in a drying-closet. The filter with the precipitate is then placed in the weighing glass and exposed for thirty minutes to the same temperature as the filter has been previously. The glass is taken out of the drying closet, immediately closed with its lid, and weighed after having been exposed to the air for exactly thirty minutes. The chief point is that the cooling process must last exactly thirty minutes, the last ten minutes in the balance case.

Influence of Hydrofluoric Acid upon Silicates.—J. B. Mackintosh.—From the *Journal of the American Chemical Society*.

Decomposition of Recently Precipitated Silver Chloride by Sunlight.—R. Hitchcock.—From the *American Chemical Journal*.

Basis for Standardising in Alkalimetry and Acidimetry.—E. Hart and Stuart Croasdale.—From the *Journal of Analytical Chemistry*.

A Simple and Portable Barometer.—G. Guglielmo (*Rendiconti d. R. Acc. dei Lincei*).—The novelty of this apparatus lies in the fact that the barometric chamber is divided into two parts by a glass cock without oil, and with a mercurial joint.

Apparatus for the Quantitative Determination of Pigments by means of their Absorption-Spectra.—T. L. Patterson.—From the *Journ. Soc. Chem. Ind.*

Modifications in Sprengel's Mercurial-Pump.—G. Guglielmo (*Rendiconti d. R. Acc. dei Lincei* and *Beiblätter Annalen Physik und Chemie*).

Two New Heating Appliances for use in the Laboratory.—Fr. Hugershoff (*Chem. Central Blatt*).—Requires the two accompanying figures.

An Electro-magnetic Thermostat.—W. F. Taylor.—From the *CHEMICAL NEWS*.

A Gas-Drying Apparatus for Elementary Analysis.—E. Sauer (*Ber. Deutsch. Chem. Gesell.*).—The somewhat complicated apparatus is shown in an appended figure.

An Apparatus for Drying at 100° in a Current of Coal-Gas.—E. Wrampelmeyer (*Landwirth Versuchstationen*).—The apparatus is shown in an accompanying figure.

A New Syphon.—F. Konther (*Chemiker Zeitung*).—For the details we must refer to the original.

Absorption Apparatus for Determining Sulphur in Iron.—J. M. Comp (*Journal of Analytical Chemistry*).

Automatic Washing Apparatus for Filters.—R. W. Wood (*Journal of Analytical Chemistry*).—No particulars are given.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xviii., No. 2.

The Assay of Antimony Ores.—Ad. Carnot.—From the *Comptes Rendus*.

Action of Carbon Monoxide upon Iron and Manganese.—M. Guntz.—From the *Comptes Rendus*.

The Chromite of California.—From the *CHEMICAL NEWS*.

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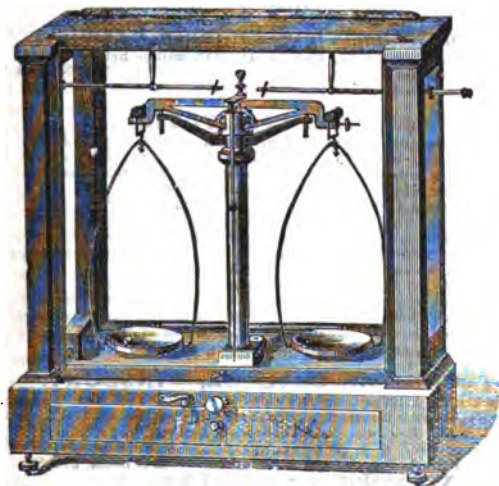


FIG. 3A

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THE CHEMICAL NEWS.

VOL. LXVI., No. 1703.

A SUGGESTED COURSE FOR THE DETECTION AND SEPARATION OF THE MORE ORDINARY ACIDULOUS RADICALS.

By FREDERICK HARRISON, M.A.

Preliminary Examination.

1. HEAT a portion on a porcelain crucible lid; if it chars much and gives off odour of burnt sugar, a tartrate or citrate may be present; if slightly, an oxalate, acetate, or some other organic acid.

2. Add dilute H_2SO_4 , and observe carefully the effect.

Effervescence, without odour .. = Carbonate.

Warm.

Red fumes = Nitrite.

Odour of sulphur dioxide = Sulphite.

Odour of sulphur dioxide and deposit of sulphur.. .. . = Thiosulphate.

Odour of sulphuretted hydrogen .. = Sulphide.

Odour of vinegar = Acetate.

Odour of bitter almonds = Cyanide.

Odour of bitter almonds and deposit of sulphur.. .. . = Ferro- or ferricyanide.

Add a few drops more H_2SO_4 , and warm with a piece of copper foil.

Red fumes = Nitrate.

Heavy metals, if found, must be boiled out with Na_2CO_3 , filtered, and the filtrate neutralised with dilute HNO_3 .

If the salts are insoluble in water, boil with KHO , filter, and neutralise carefully with dilute HNO_3 .

To a portion of the neutralised cold solution add—

I. $Ca(NO_3)_2$ in excess, and filter.

Precipitate (white) = Oxalate, sulphate, tartrate, phosphate, arseniate, borate.

II. Warm filtrate. Precipitate (white) = Citrate.

Filter while hot.

III. To filtrate add $Ba(NO_3)_2$ in excess. Filter. Precipitate = Chromate (yellow), sulphate (white).

IV. Filtrate must be divided into four parts.

(1). Add $AgNO_3$ in excess. All precipitates except curdy white must be disregarded = Cyanide, chloride, bromide, iodide.

(2). Add Fe_2Cl_6 .

Red colour discharged by HCl .. = Acetate.

Blackish = Tannate or gallate.

Blue = Ferrocyanide.

(3). Add $FeSO_4$. Dark blue .. = Ferricyanide.

(4). Reserved for proving presence or absence of cyanide by Scheele's test.

Separation of Precipitates I.—Add HCl . Agitate and filter (Filtrate A); insoluble = Oxalate, sulphate. Wash precipitates with a little cold water and percolate with dilute HCl , and neutralise filtrate with NH_4HO ; white precipitate = Oxalate. Percolate any remaining precipitate with boiling water and add to filtrate $BaCl_2$; white precipitate insoluble in HNO_3 = Sulphate.

Neutralise Filtrate A. with NH_4HO ; wash precipitate with cold water, and agitate with cold KHO ; filter and warm filtrate. White precipitate = Tartrate.

Divide any remaining precipitate, after washing, into two parts.

a. Dissolve in HNO_3 , add $(NH_4)_2MoO_4$ and warm. Yellow precipitate = Phosphate or arseniate.

To a portion of the original neutral solution add $AgNO_3$. Red = Arseniate; Yellow = Phosphate.

b. Dissolve in dilute HCl and moisten a piece of turmeric paper with solution and gently warm. Reddish colour = Borate.

Separation of III.—If yellow, chromate is present. Boil with HCl ; any insoluble white precipitate remaining is Sulphate.

Separation of IV.—(1) precipitated by $AgNO_3$. Wash precipitate and percolate with dilute NH_4HO ; neutralise filtrate with HNO_3 . White precipitate = Cyanide or chloride.

If (4) has given reaction of cyanide, boil with HNO_3 .

Any insoluble white precipitate is Chloride.

Any white precipitate insoluble in dilute NH_4HO is Bromide or iodide.

Add mucilage of starch and chlorine water. Blue = Iodide; Orange = Bromide.

To prove bromide in presence of iodide, decolourise the blue iodide of starch with excess of chlorine water and agitate with chloroform. Orange = Bromide.

A NEW METHOD FOR THE DETERMINATION OF VANADIC ACID.

By A. ROSENHEIM and C. FREIDHEIM.

THE separation of vanadic acid from those accompanying it in the so-called complex salts is attended with certain difficulties. Thus arsenic and molybdenum, after the reduction of the solution by means of sulphurous acid, have first to be removed by sulphuretted hydrogen, and then for separation from the bases the vanadic acid, after the filtrate has been oxidised with nitric acid, is separated as a mercurous salt. In presence of tungstic acid, the mixed mercury salts of both acids must be dissolved in fuming hydrochloric acid, and after separating the tungstic acid by means of water and precipitating the mercury with sulphuretted hydrogen, the vanadic acid is determined by concentrating the filtrate. Hence, it is often preferred to determine in one part of the substance the sum total of the acids by igniting the mercurous salts with an addition of sodium tungstate, and in another portion to determine the vanadic acid volumetrically, for which two methods come into consideration: the reduction of the compound by means of sulphurous acid in a sulphuric solution and oxidation of the vanadyl formed by potassium permanganate, or distillation of the same with hydrochloric acid with addition of potassium bromide, absorption of the halogen formed in consequence of reduction to vanadyl in potassium iodide, and titration by means of sodium thiosulphate.

We must, unfortunately, have recourse to such determinations by difference when, e.g., in the compounds containing phosphoric and vanadic acids a direct separation of the vanadic acid in a ponderable form is impracticable, otherwise the application of the permanganate method is limited. In presence of MoO_3 and As_2O_3 (which are also reduced by sulphurous acid) it is entirely excluded, and along with tungstic acid, as formerly shown, the recognition of the end of the titration is rendered very difficult. The method of distillation is more convenient, but, in addition to the variability of the solution of thiosulphate, it labours under the serious disadvantage that a determination of the alkali appears excluded in consequence of the addition of potassium bromide to the same portion of the substance.

In cases where a gravimetric determination of the

vanadic acid is impracticable, the above disadvantages are avoided by the following indirect method, which dispenses with any titration:—

The vanadic acid or the vanadate, in a sulphuric solution, is reduced to vanadyl by means of oxalic acid, and the carbonic acid evolved is weighed. This method, therefore, approximates to that of Fresenius and Will for the valuation of manganese ore, and that proposed by Vohl for determining chromic acid.

Berzelius mentioned that oxalic acid decomposes vanadic acid, the yellow solution passing through green to blue. But it has nowhere been shown that the reduction in fact goes on to vanadyl. This seems merely to have been inferred from the blue colour of the solution, which is the less permissible as vanadous oxide in a sulphuric solution displays a lavender-blue tone.

In order to decide if the reaction really takes place according to the equation—



a known quantity of pure ammonium vanadate (the proportion of vanadic acid in which was determined by ignition before each experiment) was decomposed by a mixture of equal vols. of solution of oxalic acid, saturated in the cold, and 10 per cent sulphuric acid, at first at a gentle heat, and afterwards at ebullition, and the carbonic acid evolved was evolved in the potash apparatus. As a decomposing apparatus there was used that first described in Rose-Finkener's handbook, recently improved by Finkener, which, though unfortunately too little known, far surpasses all other apparatus. It was also used for the analysis of the remaining compounds.

According to the above equation 182.4 parts by weight of vanadic acid ($V=51.2$, the mean of Roscoe's values [$O=16$]) should evolve 88 parts by weight of carbonic acid of 100 $V_2O_5 : 48.246 CO_2$. A series of experiments showed that this is the case, whence the above equation is correct and the previous assumption is well founded.

I.—Determination of Vanadic Acid in Vanadates.

In alkaline vanadates the water and the acid may be determined in the same portion. The ignited residue is dissolved in water,—if needful with the aid of dilute sulphuric acid, washed into the decomposing apparatus, and the carbonic acid is then liberated by means of oxalic acid.

II.—Vanadic Acid along with Phosphoric Acid.

If prior to the addition of oxalic acid and sulphuric acid dilute phosphoric acid was added to the solution, the result of the experiment was not altered. Hence the method is available for the examination of the vanadium phosphates.

III.—Vanadic Acid and Tungstic Acid.

Dilute oxalic acid acts as little upon a solution of tungstic acid acidified with dilute sulphuric acid, and leaves the colour of the precipitated acid a pure yellow as upon one which has been acidified with phosphoric acid to prevent the precipitation of tungstic acid. The latter precaution was found superfluous, as oxalic acid produces no precipitation in tungstates except in presence of much sulphuric acid. There are formed apparently stable compounds, the examination of which has been undertaken.

IV.—Vanadic Acid and Molybdic Acid.

As explained above, the examination of vanadium molybdates is attended with difficulties, as their titration with permanganate is impossible. Molybdates are not reduced by oxalic acid, whence the determination of vanadic acid on our method is practicable. The Halverscheidt method is here also available.

The method here described has the advantage over the Halverscheidt method, which is of equally general applicability, in as far as it admits of the determination of the base in the same portion.—*Zeit. für Anorganische Chemie*, vol. i., 313.

ON NATURAL PHOSPHATES.*

By J. LAINSON WILLS, F.C.S.

WHEN your President and Treasurer did me the honour to request me to read a paper on "Phosphates" before the Ottawa Field Naturalists' Club, I hesitated in complying.

"Phosphates" in a general way, as we employ the word in this locality, implies the crystallised mineral apatite, so abundant in certain parts of our Laurentian formation. The good work done by the Geological Survey has from time to time, through its officers, kept us well informed of the localities and peculiarities of the occurrence of the Canadian apatite, by valuable contributions from the pens of Sir Wm. Logan, Sterry Hunt, Vennor, Dr. Geo. Dawson, Torrance, Dr. Robert Bell, and others. At the present time, I understand that Mr. Ingall also, who has been in charge of a special study of our Canadian apatite fields, is about to terminate and publish his preliminary report; so with deference to his opportunities and approaching publication, I could not presume to undertake a paper purely on Canadian phosphates or apatites, as was proposed, but thought it might be acceptable to our members here, to give their attention to a more extended and general consideration of natural mineral phosphates, and hence the title of my paper this evening, instead of being "Canadian Apatite," is "Natural Phosphates" in a general way. My present occupation prevents me from giving much time and study to the preparation of this work, but if, by some generalisation of facts, we can awaken a healthy discussion and exchange of ideas, my humble attempt will not have been useless.

Natural phosphates owe their commercial value to the proportion of phosphoric element contained in them, and are employed as raw material for the manufacture of phosphatic fertilisers, being also sometimes applied in the natural and raw state direct to the soil by the farmer. They are also in demand for the manufacture of phosphorus, baking powders, and some other chemical products. By far the greatest demand for them, however, is made by the manure manufacturers for agricultural requirements, and this demand is yearly increasing at a very rapid rate. The occurrence of natural phosphates presents the most varied and interesting modes of formation, as may be surmised by finding their deposits, not only in nearly every geological system, but in many different series of the same system.

Now in beds which may have a fresh-water or marine origin, now appearing as hardened conglomerate or rocks, and sometimes as sand and loose gravel; then again in vein formation or pockets, sometimes amorphous, at other times crystallised.

In the matter of texture, colour, and other physical characters we find the same endless variation.

The origin of the demand for these phosphatised products is comparatively of recent date. It was only in the commencement of the present century that crushed bones were employed as a fertiliser in agriculture, and, strange to say, only then on account of the gelatin or organic matter they might contain.

The following curious statement, which appeared in a scientific journal in the year 1830, *a propos* of the employment of crushed bones in England, exposed the ignorance on the subject at that day, and reads as follows:—"As to earthy matter or phosphate of lime contained in the bones, we may disregard it. It is insoluble and indestructible, and cannot serve as a manure, even in damp soil and in immediate contact with the root-lets of the plant."

The suggestion of Liebig, to treat the bones with sulphuric acid, opened a new era, to the utilisation of phosphatic materials in agriculture, and the manufacture of artificial manure was soon established.

* A Paper read before the Ottawa Field-Naturalists' Club.

The illustrious Elie de Beaumont thus expressed himself with regard to the commencement of the mining of mineral phosphates:—"Colbert" has said that France would be lost for want of forests, and everyone perceives that without coal his predilection would soon be accomplished. In his day one would have failed to comprehend how a great country might disappear."

Natural Phosphatic Deposits.

These valuable provisions of Nature are the result of various causes and agencies familiar to the geological observer, and their contained phosphoric acid is mostly due to animal life; and when we say "due" to animal life we wish to imply that animal life is the assimilating and concentrative medium of pre-existing phosphoric acid; whether as sea and fresh-water shells, as fish and animal bones, as excreta of birds and saurians, &c., animal organisms have been from the beginning of life, and still are, the silent but mighty laboratory of Nature, never resting to collect and store up the dispersed molecules of phosphoric acid. Among such are the guano beds of recent epochs, coprolite deposits, bone beds, shell beds, &c.

Nature's operations of bringing these materials or their *débris* together to form whole geological areas are equally varied, but the estuaries and depressions of the sea-bottoms of the different and respective geological periods are recognised to have been the receptacles or store-houses of these wonderful supplies. A curious disposition to concretionary action, displayed by nuclei of certain organisms to absorb and accumulate phosphatic matter, with which the ancient seas abounded, is more easily seen in its effects than explained.

Such is the origin of many odd species of nodules, some varieties of which exist in immense quantities.

The abrupt or imperceptible, but never ceasing, operations of geological arrangement follow the aforementioned accumulations, and we then have new forms of mineralised phosphatic matter, giving rise to conglomerates, breccias, phosphatic limestone, shells and marls, sandy and ablation deposits, &c., and most of the known natural deposits of mineralised phosphate display examples of two or more of these products. For instance, the perplexities experienced just now with some of the exploratory workings of the lately-discovered Florida deposits, are chiefly occasioned by the character of these beds containing boulders, and nodules from pea size to masses of several hundred pounds in weight, fish bones, sharks' teeth, and fossil bones,—in fact *débris* from several geological epochs,—each of these materials naturally varying in purity, and therefore also in commercial value, so that the more successful enterprises may be looked for where regular and homogeneous deposits occur, or some cheap and efficient mechanical means are applied for the separation of the marketable products from the less valuable or worthless intermixtures.

The classification of natural phosphates of lime is, as remarked by Dr. Penrose in *Bulletin* No. 46 of the U.S. Geological Survey, "a matter attended with many difficulties, not only on account of the great variety of forms in which phosphate of lime occurs, but also because many varieties blend into one another, thus often rendering it uncertain to which class a special deposit should be referred," and he adopts the following classification, based mainly on the chemical composition of the deposits, and grouped under the headings thus:—

Mineral Phosphates	{ Apatites	{ Fluor-apatites
	{ Phosphorites	{ Chlor-apatites
		{ Loose nodules
	{ Amorphous nodules	{ Cemented conglomerates)
Rock phosphates	{ Phosphoric limestone beds	
	{ Guanos	{ Soluble guanos
	{ Bone beds.	{ Leached guanos

* Jean Baptiste Colbert, born 1619, Minister of Finance to Louis XIV.

We shall recognise as we proceed with the study of the various phosphatic deposits formed during the different geologic periods, that by far the greater part owe their origin to animal or organic remains, and we shall see that as soon as the organic compounds of a guano, for example, are dissipated and resolved into their elements, we may consider that the residual products, to all intents and purposes, revert to the mineral state, in accordance with the familiar expression "earth to earth."

We pass over, for the present, the guano of various localities, which, however, will be observed to lie mostly within 10 to 20 degrees of the equator.

We should remember, however, that this product has attained its zenith, both as to quality and quantity, and must cede its commercial importance ultimately to the mineral resources of phosphoric acid, which are before us for our more particular consideration.

We shall find the diagram on the wall which shows the approximate geological position or age of the different phosphate deposits, very useful to our present purpose, and we will commence with the more recently formed or mineralised products.

(To be continued).

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 21).

III.—THE ANALYSIS OF CUPRIC OXIDE.

DEPRIVED of the support of the results from cupric sulphate, Hampe's oxide determinations possess little more weight than those of any other experimenter. It will be remembered that the values of the atomic weight of copper deduced from this source have varied from 63.1 to 63.5. Such a fluctuation alone, without the confirmatory evidence which has just been given, is sufficient to cause the suspicion of an undiscovered error in cupric oxide.

With the hope of detecting the possible error, a number of analyses of the substance were made under varying conditions and with different samples of material. No difficulty was found in obtaining results varying as widely as those cited above. Part of the cause of this variation was traced to differences in the preparation, and part to differences in the temperature and tension of the surrounding air employed in ignition.† Cupric oxide ignited to constant weight at a very dull red heat lost a very perceptible amount of material upon heating to the highest temperatures which hard glass would bear. On the other hand, copper reduced by hydrogen at the lowest possible temperatures is well known to lose in weight on heating to bright redness. Some of Erdmann and Marchand's experiments (*Loc. cit.*, see p. 236, vol. lxxv.) show that the exhaustion of the tube at the time of weighing makes very little if any variation in the weight of the materials; but from others (*J. Prakt. Chem.*, xxvi., 461), as well as from the fiftieth experiment below, it would appear that exhaustion at the time of ignition introduces a somewhat more serious correction. In this last case the apparatus was necessarily rather complicated, to admit of the ignition and weighing of the copper and its oxide in a Sprengel vacuum, but the full description of the contrivance would demand more space than it is worth. In the four preceding experiments Hampe's method was carefully followed.

The mode of preparation of the cupric oxide was essentially that recommended by Hampe, and described in the

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

† Compare Bailey and Hopkins, *Jour. Chem. Soc. Trans.*, 1890, p. 269; also Schutzenberger, quoted in *Am. Jour. Sci.* [3], xxvi., 65.

Analysis of Cupric Oxide.
(Weights reduced to vacuum standard).

No. of experiment.	CuO dull redness 550°± Grms.	CuO 750°? Grms.	Cu found 400°± Grms.	Cu found 550°± Grms.	Cu found 750°? Grms.	Atomic weight of copper O : Cu = 16 : 8.
46.	2.08491	—	—	1.66405	—	63.26
47.	1.11936	1.11851	—	0.89355	—	63.29 to 63.53
48.	1.06300	1.06253	[0.8490]	—	0.84831	63.23 to [63.62]
49.	1.91703	1.91656	—	—	1.5298	63.20 to 63.29
50.	2.62410	Ignited in vacuum	—	2.0956	—	63.44
						63.37

Proc. Amer. Acad. Arts Sci., xxv., p. 199. In some cases the basic nitrate was not washed with water before ignition, and in other cases it was thus washed. In general, none but platinum vessels were used. Various slight unimportant modifications were introduced, which need not find a place here. The essential conditions to be borne in mind are the invariable use of the nitrate as the source of the oxide, and the variable temperatures employed in the ignition.

The average of results so heterogeneous in nature can naturally have no important meaning, but it is interesting to note the approximation to the old value of the atomic weight. The high value given in Experiment 48 is manifestly only a compensation of errors. From Experiments 48 and 49, the only two in which both materials were ignited at a bright red heat, 2.97909 grms. of cupric oxide yielded 2.37811 grms. of metallic copper. Computing from these data the atomic weight of copper, we obtain the value 63.313, which is comparable with the result 63.312 obtained indirectly through the synthesis of the sulphate as well as with the number 63.346 fixed upon by Hampe. The absolute identity of the first two figures must be attributed to chance, since the agreement of the individual results was not perfect.

These results again pointed to the existence of a volatile impurity in cupric oxide, but no proof was afforded that the impurity was wholly driven off at the temperature of fairly bright redness. The determination of this point, as well as of the nature of the occluded material, became a matter of great importance.

Tests for Impurities.

The first hypothesis suggested was the possible imprisonment of a small amount of water (see Müller-Erzbach, *Fahresbericht*, 1885, p. 74). To subject this hypothesis to proof, pure cupric oxide might be dried at a red heat, and reduced by means of carbon monoxide, when of course any occluded water would be set free and might be weighed.

The cupric oxide used in the execution of this plan was some of that which remained from the oxygen research. It had been prepared in the usual manner. The carbon monoxide was made from oxalic and sulphuric acids, and after a preliminary purification with caustic potash the gas was collected over water in a glass gas-holder. From this receptacle it was passed through very large amounts of potassic hydroxide, over calcic chloride and red hot platinum sponge, and finally through a flask containing sulphuric acid and two tubes containing phosphorus pentoxide, before being allowed to come in contact with the material to be reduced.

In Experiment 53—which may be taken as a type—15 grms. of the cupric oxide contained in a hard glass tube were dried at a red heat in a stream of pure air for forty-five minutes. A small weighed phosphoric oxide tube was then connected at the exit, and the current of air was continued for over an hour.

	Grms.
Weight of tube before connection	= 55.1920
“ “ after “ “	= 55.1922

The temperature changed from 15.7° to 16.8° between the two weighings, involving a correction of -0.0001 to the latter weight. The tube therefore gained only the tenth of a milligram, showing the cupric oxide to have reached a constant hygroscopic condition.

During the ensuing reduction with carbon monoxide, the drying tube was again connected with the apparatus. Before the last weighing of the tube, all carbon dioxide was expelled by pure air. The tube weighed 55.2177 grms., showing a gain of 0.0255 gm., or 0.017 per cent of the weight of the cupric oxide.

Two similar experiments led to like results.

Reduction of Cupric Oxide by Carbon Monoxide.

No. of experiment.	CuO taken. Grms.	Water formed. Grms.	Volume of carbon monoxide. Litres.	Weight of H ₂ O formed. 10 grms. CuO. Grms.
51.	6.90	0.0105	—	0.0152
52.	20.00	0.0347	—	0.0173
53.	15.00	0.0255	5.5	0.0170

Nothing in these results proved that the water was not formed from the oxidation of hydrogen or hydrocarbons possibly contained in the carbon monoxide, and indeed further examination showed that it originated from this source. The metallic copper from the last experiment was immediately oxidised by a stream of pure dry air, and once more reduced with carbon monoxide. Four litres of gas required to reduce the partially re-oxidised copper yielded 19.3 m.grms. of water. Since this water could not possibly have come from the oxidised copper, it must have been solely obtained from impurities in the carbon monoxide. The quantity closely agreed with the amount, 18.3 m.grms., which one would have expected to find from the volume of gas used, upon the basis of previous results. Considering the fact that the volumes of gas were not very accurately measured, the difference is not greater than the experimental error. Hence it may be safely concluded that the carbon monoxide contained about four one-hundredths of a per cent of hydrogen by weight, but that the cupric oxide retained no appreciable amount of water at a red heat.

Experiments 54 and 55.—The idea that some cupric nitrate might remain undecomposed in cupric oxide is evidently not a new one, for almost every experimenter upon the subject tested for nitric acid in the water formed during the reduction. It seemed possible, however, that the nitric acid might be reduced as well as the cupric oxide, and hence that the test might not be a sufficient criterion. Accordingly, 5 grms. of cupric oxide were dissolved in very pure dilute sulphuric acid, and several successive portions of water were distilled off from the mixture. After evaporation to small bulk in a platinum dish, the distillates were found to be neutral to methyl orange and acid to phenolphthalein. When the amount of standard alkali necessary to neutralise this acidity had been determined, hydrochloric acid was added and the sulphuric acid present was estimated as baric sulphate. Since the weight of baric sulphate (3.7 m.grms.) was nearly equivalent to the amount of alkali used (0.39 c.c. of a decinormal solution), since no nitric acid was found in the filtrate by the most sensitive tests, and since a very perceptible amount of copper was found there, it may be

reasonably concluded that cupric sulphate had been carried over mechanically in fine drops. A second experiment yielded like results. Hence, so far as this test was concerned, *no nitric acid was to be found in cupric oxide.*

Experiment 56.—The tendency of various oxides to hold carbonic acid even at high temperatures is well known. Thudichum (*Chem. Soc. Journ.*, 1876, [2], p. 364) has observed that, in order wholly to free cupric oxide from this impurity, it is necessary to ignite it in a vacuum. In order to test this point so far as it concerns the present investigation, the following experiment was made. After a small amount of nitric acid had been added to 12 grms. of cupric oxide, the substance was gradually brought to redness and maintained at this temperature for ninety minutes. The material was then rapidly transferred to a flask provided with a stoppered funnel and two bent tubes. One of the latter was connected with two test-tubes containing a clear solution of baric hydroxide, and the other permitted a gentle current of air to be blown through the entire apparatus. Before either baric hydroxide or cupric oxide were added, all the tubes and flasks were, of course, freed from carbon dioxide. Finally, dilute boiled hydrochloric acid was run in at the funnel tube, the cupric oxide was dissolved, and the solution was gradually brought to boiling. A slight bluish precipitate of cupric hydroxide appeared after some time in the first test-tube, while the second remained perfectly clear. The excess of baric hydroxide in the first tube was quickly neutralised with weak hydrochloric acid and phenolphthalein, and the precipitate was filtered off and washed. The absence of barium from this precipitate proved the absence of carbon dioxide from the cupric oxide.

In order to test the adequacy of the method, 3.4 m.grms. of sodic carbonate were added to the cupric chloride through the funnel tube. This quantity yielded only one-tenth the amount of carbon dioxide necessary to account for the difference between the atomic weights of copper in question, but it nevertheless produced a heavy white precipitate in both newly filled baric hydroxide tubes. The precipitate when tested showed large quantities of barium; hence the method was quite competent to decide that *the absorption of carbonic acid by cupric oxide was not the error for which search was being made.*

Experiment 57.—Although it seemed very improbable that cupric oxide could contain even traces of a higher oxide after ignition at a red heat, proof of the point was not at hand. Accordingly, 4 grms. of the substance were boiled with pure hydrochloric acid in an apparatus somewhat resembling the last one, in which all the joints were of sealed or ground glass. The vapours were driven through a reversed air cooler into bulbs containing a strong cooled solution of potassic iodide. The very small amount of iodine set free after some time was determined by means of sodic thiosulphate. This amount corresponded to 0.05 m.grm. of oxygen, but even this was undoubtedly due to copper in uncondensed spray. Eight-tenths of a milligram of potassic dichromate, subsequently added to the cupric chloride, at once set free more than double this amount of halogen in the bulbs. The method was hence shown to be adequate for the purpose. The results *prove the absence of an essential amount of any higher oxide or oxidised nitrogen from ordinary cupric oxide.*

(To be continued.)

Detection of Turkish Geranium Oil in Oil of Roses.—G. Panajotow (*Ber. Deutsch. Chem. Gesell.*).—Solution of magenta decolourised with sulphurous acid (2 c.c.) mixed with two or three drops of Turkish essence of geranium in the cold gives at first a violet blue colour and after two hours a splendid blue. Oil of roses with the same reagent gives a red colouration only after twenty-four hours.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 16th, 1892.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Lionel Cooper, 173, Marylebone Road, London, N.W.; James Robson, 1, Maxwell Street, Paisley, N.B.; John King Warry, 15, Grafton Street, Mile End, E.

The following were elected Fellows of the Society:—

As Foreign Members:—Emil Fischer, Würzburg; Carl Graebe, Geneva; Adolph Lieben, Vienna; Hugo Schiff, Florence; Th. Schloesing, Paris.

As Ordinary Fellows:—Percy Targett Adams; John W. Alcock, Arthur Edward Barrows, Horatio Ballantyne, Arthur Sanderson Bleckly, Charles Bayliss, Henry Couldery, Thomas Cockerill, Sir John Evans, K.C.B., Herbert Entwistle, John Gibson, Ph.D., John Fenton Newall, Charles James Norris, Henry Ramsden Redman, Ernest Heber Smith, Fred Whiteley, B.A.

Of the following papers, those marked * were read:—

*33. "*Contributions to an International System of Nomenclature. The Nomenclature of Cycloids.*" By HENRY E. ARMSTRONG.

An account was given of the proceedings at the recent Conference on Chemical Nomenclature at Geneva, and attention was directed to the significance of the chief resolutions.

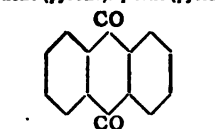
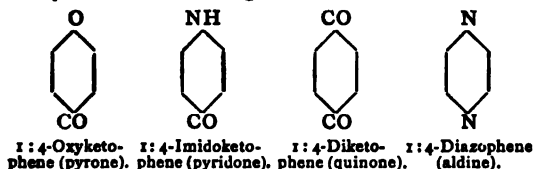
The main recommendation of the Conference may be said to be that *functional* terminations should be given to all names, *i.e.*, terminations indicative of the class to which the compound belongs. This is a principle which is familiar to English chemists through the operation of the rules laid down by the Publication Committee of the Chemical Society for the guidance of Abstractors, and one, therefore, which will readily find favour in this country.

In the case of hydrocarbons, those of the paraffin series, as heretofore, are to receive names ending in *ane*. The termination *ene* is, however, to be restricted to hydrocarbons containing carbon atoms united as in ethylene or ethene, the number of such *ethenoid* unions being indicated by a prefix, *e.g.*, propadiene = $\text{CH}_2:\text{C}:\text{CH}_2$. It is proposed that hydrocarbons containing acetylenic unions should receive names ending in *ine*; this is a somewhat unfortunate recommendation, as this termination *ine* has long been consistently applied to alkaloids by English chemists, and is an illustration of one of the difficulties met with in devising a systematic nomenclature.

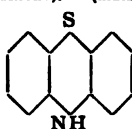
Reference was made to the discussion which arose at the Conference on the question whether carboxyl should be treated as a substituting group or no, and to the inconvenience involved in many cases in adopting the recommendation to refer acids to the hydrocarbon from which they might be regarded as derived by oxidation, a proposal which would necessitate that citric acid, for example, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{C}(\text{OH})(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, should be named methylpentanoltroic acid, numbers being added to indicate the position of the OH and CO_2H groups. The motive for this recommendation is doubtless to be found in the desire to maintain a mental picture of a relationship such as exists between alcohol, aldehyd, and acetic acid; but if it be remembered that only primary carbinols are convertible into corresponding aldehyds and acids on oxidation, and that there are no acids corresponding to secondary and tertiary alcohols and phenols, this argument does not appear of great weight. As *ol* is indicative of an OH derivative, there seems no reason why the simple word *acid* should not connote carboxyl, and why *al* should not connote COH; the names ethanal, ethanal, and ethanoic acid, or simply ethane acid, would then stand for the OH, COH, and COOH derivatives of

ethane; citric acid, on this system, would be named propanoltrioic acid or simply propanoltri-acid.

An explanation was then given at some length of the author's proposed system of nomenclature for cycloids, on which he was requested by the Conference to prepare a report. Up to the present time, the termination *ane*, applied to paraffins, has been the only one which has served to connote something more than the possession of a particular function; it has also served to convey definite information regarding the character and constitution of the compound as a whole, as definite in its way as that afforded by the term phenol applied to a particular kind of *ol* or alcohol. It is proposed to apply the term *phene* (perhaps *phen*) to all unsaturated cycloids, and *phane* (perhaps *phan*) to saturated cycloids, the number of terms or members in the cycle to be indicated by the appropriate prefix, although probably in the case of hexaphene (benzene) derivatives it would be unnecessary to use any prefix. For example, names such as furfuran, thiophen, pyrrol, indol are purely empirical and meaningless, in no way serving to indicate the similarity in structure which obtains between the compounds to which they refer, and such names cannot be countenanced much longer; a clear idea of their structure and relationship is at once given, however, by naming such compounds respectively *oxy-* (perhaps *oxo-*), *thio-*, *azo-*, and *phenazopentaphene*. Other examples are the following:—

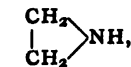


Dipheno-1: 4-diketophene
(anthraquinone).

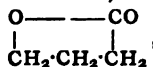


Dipheno-1: 4-thioimidophene
(thiodiphenylamine).

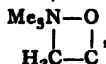
Trimethylene, regarded as a cycloid, might be *triphane*, the name *hexaphane*, or simply *phane*, being assigned to hexamethylene instead of cyclohexane, as proposed by the Conference. The *lactones*, *imines*, *betaines*—in fact, cycloids generally—may be easily named on this same principle, thereby rendering unnecessary a number of specific terminations proposed by the Conference. Thus ethenimine,—



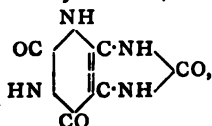
is an *imidotriphane*; the lactone,—



is a 1:2-*oxyketopentaphane*; betaine,—



is *trimethaxonoxyketotetraphane*; and uric acid, adopting the formula proposed by Medicus,—



is a *diimidodiketophenodisimidoketopentaphene*.

It is proposed to discuss the subject at length in a comprehensive paper.

DISCUSSION.

Professor Meldola, Mr. Friswell, Mr. Groves, and Mr. Page all spoke in defence of trivial names, and urged the importance of retaining them. Mr. FRISWELL thought the use of *azo* to denote nitrogen in a ring might give rise to confusion, as the term had acquired significance in connection with compounds of a different character. Mr. PAGE dwelt on the importance of giving new names, instead of transferring old ones, to new compounds. Prof. P. F. FRANKLAND thought names unnecessary, and that it would be better for the purposes of a register to use formulæ.

The PRESIDENT said that we must keep in mind that such systematic names as had been suggested were really names of formulæ rather than names of substances. Thus, a name had been suggested for uric acid on the assumption that *Medicus's formula correctly represents the constitution of the acid*. He thought it did, and so do most chemists, but some do not, and for them the name suggested will not be the name of uric acid. Again, a new substance is discovered; its discoverer has no doubt as to its constitution, and gives it the corresponding name—it is written about, is used for preparing other substances, perhaps comes to be made on a large scale, but after a time it is found not to have the constitution indicated by its name: it must then get a new name, and its old name will be given to a substance now supposed to have the constitution it indicates. Hence will arise confusion, for when we come across the word in reading we may have some difficulty in ascertaining which substance is meant. Mr. PAGE gave an instance of this kind of confusion—the old hyposulphite had its name correctly enough changed to thiosulphate, but unfortunately the old name, supposed now to be free, was given to Schützenberger's salt. The best way out of this confusion is to abandon the name hyposulphite altogether, and speak of thiosulphates and hydrosulphites. With a rigorously systematic nomenclature we should have no such resource, for the old misapplied name would be wanted for another substance, and confusion would be unavoidable, except by adding in all such cases words sufficient to identify the substance. These words would then be the *name*; the systematic name would be a statement of our opinion as to the constitution. In reference to the objection to the termination *ine* for hydrocarbons with an acetylene union, we could get over this by returning to the old termination *a* or *ia* for bases—morphia, quinia, methyllia, &c. He thought that in translating the French names into English we should as far as possible drop the final *e*, and so bring our pronunciation nearer that of our brethren on the Continent. When the French nomenclature of salts was first introduced into this country, some chemists dropped the final *e* in sulphate, nitrate, &c., and, no doubt, pronouncing these words with the *a* of *hat*, not as we now do with the *a* of *kate*. The confusion would be serious with *ane*, *ene*, *ine*, for an Englishman, unless carefully trained and warned, would be sure to pronounce *ane* almost exactly as a Frenchman pronounces *ène*, and *ene* almost exactly as a Frenchman pronounces *ine*. This would be avoided if we were to spell *an*, *en*, *in*, for, although the pronunciation would not be identical with the French, there would be no risk of mistaking the one for the other, except perhaps in the extreme form of south English, in which *an* comes so near *en* as to appear almost identical to those unaccustomed to that dialect.

Mr. GROVES quoted words such as *fat* and *fate* to show that in English we could not dispense with the terminal *a*.

Dr. ARMSTRONG, in reply, said that notwithstanding its disadvantages, a system of nomenclature based on formulæ had become a necessity of the times; trivial names would necessarily still be used, but their use would probably become more and more restricted to substances in daily use. He was satisfied that within a very few years a system of nomenclature would be devised, and, therefore, it was all important that we should contribute our due share to it, and do our best to establish as good a

them as possible adapted for use by English-speaking chemists.

34. "The Production of Pyridine Derivatives from the Stone of Triacetic Acid." By N. COLLIE, Ph.D., and S. MYERS.

The authors have studied the compound obtained by interaction of ammonia and triacetic lactone referred to by one of them in a previous communication (C. S. *Trans.*, 1891, 617); they show that most probably it is an *α*-dihydroxy-*α*-picoline rather than the imidodiketone compound isomeric therewith. After various attempts to displace the oxygen by chlorine, they at last succeeded in effecting this by means of phosphorus oxychloride; the product possessed all the properties of a dichloropicoline, and when passed together with hydrogen over heated zinc dust gave *α*-picoline boiling at 128–129°. The melting-points of the platin- and auri-chlorides, and of the picrate prepared from the synthetic alkaloid, were found to be considerably higher than those noticed by former workers, but substances having the same melting-points were ultimately obtained from pure *α*-picoline, prepared by heating pyridine methiodide. The following are the melting-points observed:—

	B. p.	Platin- chloride. M. p.	Auri- chloride. M. p.	Picrate. M. p.
Picoline from lactone ..	about 128°	216–217° (221–222° corr.)	183–184° (186–187° corr.)	169–171° (172–173° corr.)
Picoline from pyridine ..	127–129°	do.	do.	do.

The platinichloride prepared from a specimen of bone-oil picoline (b. p. 128–129°), after more than twenty recrystallisations, melted at 210–211°, and the melting-point could not be further raised.

*35. "The Fermentation of Arabinose by *Bacillus Ethaceticus*." By PERCY F. FRANKLAND, F.R.S., and JOHN MACGREGOR.

The products are qualitatively the same as were obtained in the fermentations of glycerol by the same organism, consisting of ethyl alcohol, acetic acid, carbon dioxide, hydrogen, and traces of succinic acid, together with another acid, which was not identified, although its carbon dioxide equivalent was determined. When, however, the fermentation is conducted in a space closed by a mercury seal instead of cotton-wool, a notable proportion of formic acid also occurs amongst the products. The carbonic anhydride and hydrogen are evolved in equimolecular proportions. When the fermentation is conducted in a closed space, the products are formed approximately in the proportions—



the formic acid, as well as the carbon dioxide and hydrogen found, being all collected together as formic acid in this statement.

In the fermentations conducted in flasks plugged only with cotton-wool, on the other hand, the alcohol and acetic acid were in the proportion $2\text{C}_2\text{H}_6\text{O} : 3\text{C}_2\text{H}_4\text{O}_2$. It appears therefore that in the fermentation of arabinose by *Bacillus ethaceticus* the proportion of acetic acid to alcohol is greater than in that of dextrose, and still greater than in that of mannitol and glycerol, but less than in that of glyceric acid.

*36. "Resolution of Lactic Acid into its Optically Active Components." By T. PURDIE, Ph.D., B.Sc., and J. WALLACE WALKER, M.A.

The object of the investigation described in this paper is to show by direct analytical methods that ordinary lactic acid, in accordance with the theory of Van't Hoff and Le Bel, is composed of two oppositely active constituents. Applying the method of Pasteur, which depends on the difference of solubility of the alkaloid salts of active isomeric acids, the authors have resolved ordinary

lactic acid into a dextro- and a lævo-acid by means of the strychnine salt. The strychnine salts of both the active acids are crystallisable, but the strychnine lævolactate is considerably less soluble in water than its isomeride. By the fractional crystallisation of the mixed salts and the removal of the strychnine from the crystals and mother-liquors by means of ammonia or barium hydrate, they obtained salt solutions which were respectively dextro- and lævo-gyrate. The dextrogyrate ammonium salt yielded a dextrogyrate zinc salt having the same composition and solubility as zinc sarcocollate. Its specific rotation, +5.63°, indicated, however, that it contained some inactive lactate. A dextrogyrate zinc ammonium salt, $\text{C}_6\text{H}_{10}\text{O}_6\text{Zn} \cdot \text{C}_3\text{H}_7\text{O}_3\text{NH}_4 \cdot 2\text{H}_2\text{O}$, crystallising in well-defined prisms, and having a specific rotation of about +6.49° in an 8½ per cent solution, was also prepared. No corresponding salt of ordinary lactic acid could be obtained. The dextrogyrate salts yielded a lævograte acid, which, like sarcocollatic acid, yielded an oppositely active anhydride.

The lævograte salts obtained from the more soluble strychnine salts were mixed with much inactive lactate, which, however, was mostly eliminated by fractional crystallisation of the zinc salt. Lævograte zinc and zinc ammonium salts, similar in composition to the corresponding dextrogyrate salts, were also prepared. The specific rotation of the lævograte zinc salt was similar in amount to that of the oppositely active isomeride, that of the zinc ammonium salt being somewhat lower, owing to the presence of inactive salt.

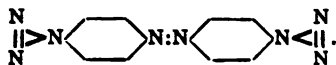
A special experiment proved that the quantities of oppositely active acids separated from each other by means of the strychnine salt possessed equal amounts of optical activity.

When the dextro- and lævograte zinc salts with 2 mols. of water were mixed, the less soluble inactive zinc salt was at once precipitated. Fermentation lactic acid is thus shown by analysis to consist of two oppositely active isomeric acids, one of which is identical with dextrogyrate sarcocollatic acid, and the other with the lævograte acid obtained by Schardinger (C. S. *Abstr.*, ix., 1891, 666) by the bacterial decomposition of cane sugar.

37. "A Method for Determining the Number of NH_2 Groups in certain Organic Bases." By R. MELDOLA, F.R.S., and E. M. HAWKINS.

In the course of an investigation upon which the authors are still engaged, the question has arisen as to whether a certain base contains two NH_2 groups, or one NH_2 and one NH group. The ordinary methods of acetylating, diazotising, the formation of azo-derivatives, &c., having given ambiguous results, the authors have made experiments to ascertain whether in such cases the azoimide could be formed by Griess's method (action of ammonia on the diazoprobromide), as the determination of nitrogen in the pure product would leave no doubt as to the number of NH_2 groups which had been diazotised. As a test case they have started with the symmetrical *p*-diamido-azobenzene, $(\beta)\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 (\beta)$: this base is not easy to prepare in quantity by the methods usually described, and it was only after many experiments that they found the method patented by the Soc. Anon. des Mat. Color. de St. Denis (Eng. Pat., 1579, January 29, 1890) to be the most direct, although the yield it affords is not very large. According to this method, diazotised paranitranilin is combined with β -naphtholdisulphonic acid in alkaline solution (the G- and R-salts need not be separated), and the purified colouring matter is reduced by boiling with caustic soda and grape sugar. The base thus prepared was purified, diazotised in the presence of chlorhydric acid, and converted into the tetrazoprobromide in the usual way. The latter, which forms an orange crystalline powder, was allowed to remain for some hours in contact with cold dilute ammonia. The product, after several crystallisations from alcohol, forms lustrous silvery scales, melting sharply at 142°. A little above this

temperature it explodes. Analysis confirmed the formula—



Calculated. . . . C, 54.54; H, 3.03; N, 42.42 p. c.
Found C, 54.58; H, 3.33; N, 42.30 "

The substance is readily soluble in benzene, slightly soluble in petroleum, and crystallises beautifully from hot glacial acetic acid. Nitric acid or sodium nitrite added to the acetic acid solution produces an evanescent magenta-red colouration. The compound is easily reduced both by acid and alkaline reducing agents to paraphenylenediamine; the authors were unable to convert it into a diphenyl base by means of cold stannous chloride.

The method described is recommended for compounds containing NH_2 groups in different nuclei, as the azoimides are well characterised and easily crystallisable compounds. The method which is sometimes adopted, viz., the displacement of the NH_2 groups by a halogen, of course gives the same information, but in many cases this process does not work satisfactorily, and in laboratories where the vacuum method of determining nitrogen is in constant use, the determination of this element is a much simpler operation than the determination of a halogen.

38. "The Existence of Two Acetaldoximes." Second Notice. By WYNDHAM R. DUNSTAN and T. S. DYMOND.

The authors are now able to furnish further information on the change undergone by acetaldoxime when heated (*cf. Chem. Soc. Trans.*, 1892; *Proc.*, 1892, 89). The melting-point of the pure crystals, thoroughly freed from adhering crystals by pressure between blotting-paper, is 46.5° (corr.), the determination being made in a capillary tube. When these crystals are melted and heated at 100° for a few minutes, no apparent chemical change takes place, but the liquid cannot now be crystallised until 13° (corr.). A similar change in the original substance takes place more slowly at 50° , the freezing-point of the liquid gradually falling to the minimum of 13° ; even at 20° this alteration slowly takes place, the crystals gradually melting and furnishing at last a liquid freezing at 13° . At temperatures above 100° the change is very rapid, but unless decomposition occur the freezing point of the resulting liquid never falls below 13° , however long the heating may be continued. This liquid, on exposure at 0° , is very slowly entirely re-converted into the original aldohime melting at 46.5° .

At first it was thought that the liquid crystallising at 13° entirely consisted of a new modification of acetaldoxime. This, however, is not the case, and so far it has not been possible to crystallise the new modification or even to obtain it in a pure state. The liquid never completely solidifies at 13° . On separating the crystals from the liquid and thoroughly drying them, they melt at 46.5° , and therefore consist of the original substance. The liquid from which these crystals were separated now freezes at a lower temperature than 13° , producing more crystals of the original substance, but on cooling the new residual liquid the freezing-point is found to have risen, and on repeating the operation the freezing-point of the separated liquids rises each time, so that by degrees the whole of the substance is obtained in its original form (m.p. 46.5°).

It is therefore evident that the liquid freezing at 13° is a solution of the original hydroxime in a new liquid modification. This liquid modification cannot be obtained pure, because, on the one hand, there is a limit to the amount of it which can be produced by heating the solid, whilst on the other hand, although a somewhat stronger solution can be made by removing the crystals which separate at 13° , this operation cannot be repeated so as to produce stronger and stronger solutions and finally the pure substance, because at these low temperatures the liquid modification gradually undergoes conversion into the original aldohime (m.p. 46.5°); and, therefore,

solutions containing less and not more of the new modifications are obtained.

The process by which the new acetaldoxime is formed is therefore a reversible one.

There is only a small difference (0.003) between the relative density of the original substance at its melting-point and that of the solution (t.p. 13°) at the same temperature.

Determinations by Dr. Perkin of the magnetic rotations of the two liquids also exhibit only slight differences; the molecular rotation of the liquid freezing at 46.5° being 3.400 and that of the liquid freezing at 13° , 3.401 .

The molecular weight of the original crystals determined by Raoult's method, using benzene as the solvent, is nearly twice as great as that corresponding with the formula $\text{C}_2\text{H}_5\text{NO}$ (59). The same result was obtained with the solution (t.p. 13°). The two modifications, therefore, have the same molecular weight. When acetic acid is used in the determination of the molecular weight instead of benzene, both the crystals and the solution give numbers closely agreeing with that representing the weight of the gaseous molecule $\text{C}_2\text{H}_5\text{NO}$.

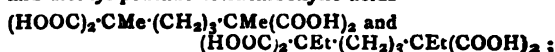
The two modifications of acetaldoxime are therefore isomeric and not polymeric.

When acted on by acetic chloride or anhydride, acetaldoxime is stated to furnish acetonitrile and not an acetyl derivative. In the light of the observations recorded above, it seemed not unlikely that previous observations have been made with a substance consisting largely of β -acetaldoxime. Experiments have therefore been made with α -acetaldoxime (m.p. 46.5°), under such conditions that isomeric change into the β -modification cannot occur during the interaction, as it undoubtedly would if acetic chloride or anhydride were caused to act in the ordinary manner. In this way the authors have obtained what appears to be *acetyl- α -acetaldoxime*. The crystals were gradually dissolved in acetic anhydride, cooled to 0° , and after some hours the liquid was poured into a weak alkaline solution, when an oily liquid separated. This liquid cannot be crystallised, and it does not distil without decomposition. When heated with water it decomposes into acetic acid and acetaldoxime. Solid potash converts it into ammonia and acetic acid. The properties of this compound are being further investigated.

The facts now recorded demonstrate the existence of two isomeric acetaldoximes which seem to correspond in their principal properties with the two benzaldoximes, which, however, are far from stable. The isomerism of the benzaldoximes is now generally adjudged to be stereochemical: although it is probable that this is also true of the acetaldoximes, the authors consider that further experiments are needed before it can confidently be asserted that the isomerism is incapable of a structural explanation. Although it might at first seem that the small difference observed in the magnetic rotations is in harmony with the stereochemical theory, when the magnetic rotations are calculated for the possible structural formulæ, it is found that the differences are also small and are actually too slight to afford trustworthy criteria of structural isomerism.

39. "The Dissociation Constants of Organic Acids." By JAMES WALKER, D.Sc., Ph.D.

The author has determined the dissociation constants of various alkyl derivatives of pimelic acid; of dimethyl- and diethyl-pentane-tetracarboxylic acids—



of several carboxyl derivatives of the polymethylenes; of citric, aconitic, and tricarballic acids; and of a number of acid ethereal salts of dibasic organic acids, $\text{R'OO} \cdot \text{R''} \cdot \text{COOH}$. He finds that the introduction of an alkyl group into the molecule of pimelic acid has little influence on the strength of the acid, which corresponds with Walden's observations on the substituted glutaric

acids. The closing of a carbon chain to form a polymethylene ring is not accompanied by any marked change in the constant. The constants of tricarballic, aconitic, and citric acids, form a series parallel to that formed by the constants of succinic, fumaric, and malic acids, their values being considerably greater, however, corresponding with the greater number of carboxyl groups in the molecule.

Ethyl hydrogen salts of dibasic acids have constants equal in general to about half the constants of the corresponding dihydrogen salts. Exceptions to this rule are only found in the case of dibasic acids with constants abnormally high. Methyl hydrogen salts possess constants somewhat greater than those of the corresponding ethyl hydrogen salts, so that the group COOM has a somewhat more marked acid character than the group COOEt.

40. "Notes on the Preparation of Alkyl Iodides." By JAMES WALKER, D.Sc., Ph.D.

The author describes a method for the convenient and rapid preparation of considerable quantities (500—1000 grms.) of methyl or ethyl iodide from iodine, methyl, or ethyl alcohol, and a mixture of red and yellow phosphorus. The apparatus employed is a modification of a fat extraction apparatus, by means of which the iodine is dissolved by the condensed alcohol or iodide, and runs into a vessel containing the phosphorus and alcohol. The method requires little attention, and gives a good yield—570 grms. of ethyl iodide from 500 grms. of iodine. It may also be applied to the preparation of higher iodides.

41. "An Examination of the Products obtained by the Dry Distillation of Bran with Lime." Preliminary Communication. By W. F. LAYCOCK, Ph.D., and F. KLINGEMANN, Ph.D.

Considerable quantities of bran and unslaked lime, in the proportion 1 to 2 by weight, were subjected to dry distillation. The resulting distillate consisted of a black oil floating on an aqueous solution. The aqueous solution smells of herring-brine and contains large quantities of ammonia. On boiling the solution gases are evolved, which burn on ignition with a slightly luminous flame. Amines and furfuran are probably present.

The oil after repeated fractionation was found to have no constant boiling point. Analysis of different fractions showed that they all contained about 4 per cent of nitrogen.

They were treated successively with (1) water, (2) sodium bisulphite solution (the resulting solution contained aldehydes or ketones), and (3) phenylhydrazine. The oils which remained unaffected by this treatment were distilled three times over excess of sodium and eventually fractionated. Analysis showed that the percentage of nitrogen had not been affected to any great extent, but that the substances containing oxygen had been for the greater part destroyed. The percentage of carbon was higher than in the original oil, and, judging from the behaviour of the oil towards agents, indifferent substances, probably hydrocarbons, were present. The oil is evidently a complex mixture, and fractional distillation appears to be of limited use as a means of isolating its constituents.

42. "The Atomic Weight of Palladium." By G. H. BAILEY, D.Sc., Ph.D., and THORNTON LAMB.

The authors have been engaged during the past three years on the investigation of palladium salts and the re-determination of the atomic weight of palladium.

After an examination of the values obtained from various salts, especially potassium palladium chloride (the salt used by Berzelius) and the palladammonium salts, they come to the conclusion that the most reliable substance for the estimation of the atomic weight is palladammonium chloride, $\text{Pd}(\text{NH}_3\text{Cl})_2$. They prepared a series of fractions, and determined the relation between the weight of salt taken and the palladium and chlorine obtained on reducing the compound in hydrogen. The

mean of their results from the palladium is 105.46. They point out that the chlorine determinations afford far from accordant values, owing to irregularities arising in the course of the decomposition of the salt and to the difficulty of arresting the whole of the ammonium chloride. The atomic weights of all the platinum metals have now undergone revision, and it is interesting to note that the relations already pointed out by Seubert (*Liebig's Annalen*, ccxii., 279), are even more pronounced when the new value is introduced in place of that obtained by Berzelius (106.35).

Ruthenium.	Rhodium.	Palladium.	Silver.
101.4	102.7	105.5	107.7
Osmium.	Iridium.	Platinum.	Gold.
190.3	192.5	194.3	196.7
Differences ..	88.9	89.8	88.8
			89.0

43. "The Action of Sulphuryl Chloride on Acetorthotoluidide and Acetparatoluidide." By W. P. WYNN, D.Sc.

1:2:5-metachloracetorthotoluidide is almost the sole product of the interaction of equal weights of sulphuryl chloride and acetorthotoluidide when the latter is suspended in five times its weight of carbon bisulphide. 1:2:5-dichlorotoluene, obtained by hydrolysis of pure potassium 1:2:5-dichlorotoluenesulphonate, boils at 200° under 770 m.m. pressure; on sulphonation with 10 per cent anhydrosulphuric acid at 70—100°, this dichlorotoluene yields a single sulphonic acid, the *barium* (+ H_2O), *potassium* and *sodium* (+ $\frac{1}{2}\text{H}_2\text{O}$) salts of which are described; the *chloride*, $\text{C}_6\text{H}_2\text{MeCl}_2\cdot\text{SO}_2\text{Cl}$, crystallises in large tables melting at 43°.

When acetparatoluidide, suspended in carbon bisulphide, is treated with an equal weight of sulphuryl chloride, 1:3:4-metachloracetparatoluidide is the chief product; small quantities of 1:3:4:5-dichloracetparatoluidide and the tri- and tetra-chloro-derivatives being also formed. The corresponding chlorotoluidines are converted into chlorotoluenes by Sandmeyer's method, and these may be separated partly by fractional distillation and partly by fractional sulphonation, since parachlorotoluene is almost exclusively sulphonated by 100 per cent sulphuric acid, 1:3:4-dichlorotoluene by 5 per cent anhydrosulphuric acid, and 1:3:4:5-trichlorotoluene by 10 per cent anhydrosulphuric acid at temperatures below 100°. 1:3:4-Dichlorotoluene, on treatment with 5 per cent anhydrosulphuric acid, yields sulphonic acid, the *barium* (+ H_2O), *potassium* and *sodium* (+ H_2O) salts of which are described; the *chloride*,—



crystallises in long, probably monosymmetric prisms melting at 82°. On hydrolysis of the potassium salt, pure 1:3:4-dichlorotoluene is obtained, boiling at 207° under 764 m.m. pressure. 1:3:4:5-Trichlorotoluene, on treatment with 10 per cent anhydrosulphuric acid, yields a single sulphonic acid, of which the *barium* (+ H_2O), *potassium* and *sodium* (+ $\frac{1}{2}\text{H}_2\text{O}$) salts are described; the *chloride*, $\text{C}_6\text{H}_2\text{MeCl}_3\cdot\text{SO}_2\text{Cl}$, crystallises in short, slender needles, melting at 88°. On hydrolysis of the potassium salt, 1:3:4:5-trichlorotoluene is obtained; this melts at 42.5°, boils at 245.5—247° under 768 m.m. pressure, and, on oxidation with dilute nitric acid, yields the corresponding trichlorobenzoic acid melting at 203°.

The action of sulphuryl chloride, therefore, corresponds very closely with that of chlorine on acetortho- and acetpara-toluidide, as described by Lellmann and Klotz (*Annalen*, ccxxxi., 310).

Orthochlorotoluene, on sulphonation with 100 per cent sulphuric acid at 60°, seems to yield only one sulphonic acid, the *barium* (+ H_2O), *potassium* (+ $\frac{1}{2}\text{H}_2\text{O}$) and *sodium* (+ H_2O) salts of which are described; the *chloride*, $\text{C}_6\text{H}_3\text{MeCl}\cdot\text{SO}_2\text{Cl}$, crystallises in long, flattened, irregularly developed prisms melting at 59°.

Metachlorotoluene, under like conditions, seems to

form only one sulphonic acid, the *barium* ($+H_2O$), *potassium* and *sodium* ($+H_2O$) salts of which are described; the *chloride*, $C_6H_5MeCl \cdot SO_2Cl$, crystallises in brilliant, long, orthorhombic prisms melting at 53° .

Parachlorotoluene is less readily sulphonated by 100 per cent sulphuric acid than its isomerides, and yields two isomeric sulphonic acids, which have not yet been completely separated. Two series of salts are described, one of which is beyond question derived from the mixed acids, as shown by an investigation of the sulphochloride. The results obtained agree in the main with those of Vogt and Henninger (*Ann. Chim. Phys.*, [4], xxvii., 130), and tend to show that the 1:2:4-isomeride, identified by conversion into the 1:2:4-parachlorotolueneortho-sulphonamide described by Heffter (*Annalen*, ccxvi., 209) is the minor product of sulphonation.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, July 4, 1892.

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE following were elected Members of the Royal Institution:—Walter Palmer, B.Sc., and the Hon. Sir Alfred Wills.

The Special Thanks of the Members were returned for the following Donations for carrying on investigations on Liquid Oxygen:—Professor Dewar (Grant from Royal Society), £300; Ludwig Mond, £120; Hugo Müller, £50.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

NOTICES OF BOOKS.

Directory and List of Products of the Chemical Industries of the German Empire. (Adressbuch und Waarenverzeichnis der Chemischen Industrie des Deutschen Reiches. 8vo., pp. 1164, besides Appendix). Edited by OTTO WENZEL, General Secretary of the Society for the Protection of German Chemical Industries. Third Edition. 1892. Berlin: R. Muckenberger.

THE goodly volume before us may be pronounced at once a movement of persevering industry and of enterprise. No small part of the work, including the title-page, the table of contents, the index of subjects, and the catalogue of chemical products, is drawn up in five languages—German, English, French, Spanish, and Italian. In a large majority of cases the English names of products, &c., are perfectly correct. In a few cases errors have slipped in, such as "sweaty foot" for "sweaty feet." The English chemical nomenclature adopted is not that recognised by the Chemical Society and used in the *CHEMICAL NEWS*, but an older and less compact system. Thus Herr Wenzel writes "ortho-formiate of ethyl," when we should say "ethyl ortho-formiate." We do not in this country write "jodide," but "iodide."

We notice with pleasure that the author does not indulge in the perplexing medical pharmaceutical terminology which is little understood outside of Germany, and which causes non-German readers to confound, e.g., chlorates and chlorides, bromates and bromides, &c. Typographical errors are creditably rare in a book written in a variety of languages and dealing chiefly with technical matter.

The work, after the detailed index, gives an index to advertisements, a list of the local associations for protecting the interests of chemical industrialists, a list of the chemical manufactories of Germany, with their trade-

marks, if any, of the analytical, technical, agricultural, and metallurgical laboratories, experimental stations, &c.

Then follows the list of chemicals, with the names and addresses of the manufacturers, the ethereal oils and essences, including compound oils for perfumery (N.B. not "composed oils"), essence not causing turbidity (not "never cloud essences"), manures and cattle-foods, explosives, colours (a most numerous category), fats, oils and lubricants, varnishes, lacquers and polishes (not lakes!). Matlack had better have been rendered by "dead varnish" than by dull varnish; caoutchouc and gutta-percha wares, resin, pitch and tar, cements, gums and thickeners, coal, charcoal and carbon preparations, mineral waters (here "gicht-wasser" should have been translated not "gouty-water," but "gout-water"), pharmaceutical preparations, photographic requisites, polishing and cleansing materials, soaps, perfumes and cosmetics, waxes and articles of wax, matches, fuses and fireworks.

No one, we think, on carefully reading over this portion of the work before us, can fail to be struck with the enormous magnitude and variety of the German chemical trades and arts, especially if he reflects that the greater part of all this has been the creation of the last half-century. We see here the outcome of that theorising which so many thoughtless persons have derided as useless.

The next portion of the work gives a list of raw materials and of intermediate products, with the addresses of the producers or merchants.

"Blighted corn" is scarcely a good English expression for Mutter korn; it should be "ergotised rye."

Another important section of this Directory includes the agencies, wholesale houses, export and import houses in Germany and other countries.

The towns are given in alphabetical order, and under each the addresses of the houses concerned. Lastly comes the advertisement department.

The entire compilation will be eminently useful to manufacturers and merchants, not merely in Germany, but in all industrial countries.

The entire getting up of the book does very great credit to the publisher, and we hope that the sale will—as it deserves to do—prove amply sufficient to remunerate them for the very heavy outlay which they have evidently incurred.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Analytische Chemie.
Vol. xxxi., Part 2.

Stability of Solutions of Potassium Permanganate.—R. W. Oddy and J. B. Cohen.—From the *Journal of the Society of Chemical Industry*.

Volatility of Sulphuric Acid at Common Temperatures.—G. A. Konig, also A. Colefax.—From the *CHEMICAL NEWS*.

Prevention of a Violent Escape of Oxygen.—M. Landolt (*Berg. und Hütten. Zeitung*).—On preparing this gas from a mixture of potassium chlorate and manganese peroxide, the author recommends an addition of potassium chloride, e.g., the residues of a former operation.

Detection of Free Chlorine in Hydrochloric Acid. M. Kupferschläger.—From the *Bull. de la Soc. Chimique*.

Preservation of Sulphuretted Hydrogen-Water.—A. Schneider (*Pharm. Central Halle*).—The author recommends black glass bottles with glass stoppers thickly smeared with vaseline.

Electrolysis.—Thomas Moore.—From the *CHEMICAL NEWS*.—There is added a continuation of the subject by E. F. Smith (*American Chemical Journal*) on the separation and determination of different metals in presence of normal phosphoric acid.

Separation of Ferric Oxide from Alumina.—F. Beilstein and R. Luther.—The process depends on the unequal solubility in water of the basic ferric nitrates and those of aluminium. The precipitated oxides are dissolved in nitric acid, the solution is evaporated on the water-bath, and the residue is allowed to stand on the bath until acid vapours cease to escape. For their detection a test-tube filled with snow or with a freezing mixture is held over the capsule, and the reaction of the water condensed on its sides is examined. The contents of the capsule are covered with hot water, the solid residue is duly crushed up in the water, and—if a small capsule was used—the whole is rinsed into a beaker in which the mixture is boiled for ten minutes. It is then allowed to cool, from 2–3 c.c. of a 10 per cent solution of ammonium sulphate is added, and after depositing the basic iron nitrate is filtered off. As this salt very readily clogs the filter, it is better not to suck the precipitate dry with the water-air pump, but it is collected upon a double filter or filtered through a layer of asbestos placed upon a platinum cone. The precipitate is washed—preferably first by decantation—with a cold dilute solution of ammonium nitrate and finally with a similar hot solution. As it is never practicable to scrape off the precipitate quantitatively from the capsule, the adhering parts are dissolved in dilute hydrochloric acid and reprecipitated with ammonia. The liquid which first passes through often contains a little ferric oxide, although it is perfectly clear and colourless. The detection of iron is easy if we first acidulate the filtrate with hydrochloric acid and then add potassium sulphocyanide. The subsequent portions of the filtrate, however, give no reactions for iron. The first portion of the filtrate (about 100 c.c.) is once more passed through the same filter when it is found perfectly free from iron.

The Electric Conductivity of the Solutions of Organic Acids and of their Salts.—D. Berthelot (*Annales de Chimie and Comptes Rendus*).

Detection of Phloroglucine.—M. Weselsky, further studied by M. M. Cazeneuve and Hugouneq.—From the *Bull. Soc. Chimique de Paris*.

Reagent for Hydrocarbons of the Acetyl Series.—A. Béhal (*Bull. Soc. Chimique de Paris*).

The Ultimate Determination of Carbon and Hydrogen.—J. Kjeldahl (*Meddelelser fra Carlsberg Laboratoriet tredje Bind.*).—This paper will be inserted at length.

Solubility of Acid Potassium Tartrate.—Ch. Blarez.—From the *Comptes Rendus*.

Rotatory Power of Camphor dissolved in Oils.—P. Chabot.—From the *Comptes Rendus*.

Quantitative Determination of Phenol.—L. Carré.—From the *Comptes Rendus*.

Determination of Phenols.—J. Messinge and G. Vortmann (*Ber. Deut. Chem. Gesell.*).—The authors propose a volumetric process depending on the formation of iodised phenols. From 2–3 grms. of the phenol are dissolved in soda-lye (free from nitrite), so that to 1 mol. of phenol at least 4 mols. of soda are present. The solution is made up to 250 or 500 c.c., and of this solution 5 or 10 c.c. accurately measured are put in a small flask heated to about 60°, and decinormal solution of iodine is added until the liquid is coloured a deep yellow by excess of iodine, when a precipitate appears on shaking. The liquid when cold is acidified with dilute sulphuric acid, the solution made up from 250–500 c.c., and the excess of iodine is determined in an aliquot part of the filtrate with a solution of sodium thiosulphate standardised to the decinormal solution of iodine. The proportion of

phenol is determined from the proportion given below and the iodine consumed.

Consumption of I.		Colour of precipitate.	
1 mol. phenol,	6 atoms I.		scarlet.
1 " thymol,	4 " "		brownish red.
1 " β -naphthol,	3 " "		dirty green.
1 " salicylic acid,	6 " "		red.

Detection of Pathogenic Bacilli.—K. Ilkewitsch (*München Med. Wochenschrift*).—For detecting the bacilli of tubercle in milk 20 c.c. of the specimen are coagulated with dilute citric acid, the whey is removed, and the caseine inclosing the bacilli is dissolved in a solution of sodium phosphate. The solution thus obtained is well shaken up with 6 c.c. of ether to counteract the action of the fat globules upon the bacilli, the mixture is allowed to stand for the evaporation of the ether, and the mixture is whizzed by means of a modified "lacto-krit" (3600 revolutions per minute). The vessel for the reception of the milk consists of a copper tube, for the bottom of which there is substituted a little basin ground to fit, into which, after the end of the centrifugal process, there is let down a minute copper globe not reaching quite to the bottom (distance 3 m.m.) in order to cover the sediment in the basin. If the centrifugal process does not last longer than fifteen minutes the great majority of the bacilli in the coagulum sink to the bottom of the basin. The copper globe secured to a thread is now let down to the bottom, the supernatant liquid is poured away, the sediment is taken out, distributed into several glasses, stained according to the Ziehl process, and examined with the microscope. With the aid of this method the presence of the bacilli of tubercle were detected with certainty in milk, even when the method of infection gave no results. In examining drinking-water Finkelburg did not succeed in the direct demonstration of Eberth's bacillus in the water by plate cultures, though he succeeded by using the precipitate obtained in the sedimentation apparatus (see *Centralblatt für Allgemeine Gesund.*, x., p. 92).

Detection of Alum in Bread.—M. Schuhmacher-Kopp (*Chemiker Zeitung*).—The author uses the tincture of logwood proposed long ago by Horsley.

Contributions to the Determination of Sugar and Tannin in Wines.—J. H. Vogel.—The author considers it necessary before the determination of sugar, whether in white or red wines, to remove disturbing constituents, especially tannins and colouring-matters.

The Degree of Fineness of Flour.—M. Holz (*Pharm. Central Halle*).—The author uses alcoholic solution of phloroglucine in a 1 per cent solution followed by concentrated hydrochloric acid.

Detection of Sulphuretted Hops.—E. Prior (*Bayr. Brauer-Journal*).—Each experiment is effected as follows:—10 grms. hops are covered in a flask holding 500 c.c. with 200 c.c. of distilled water, which is allowed to remain in contact with the hops for half-an-hour, shaking frequently. The watery infusion is then passed through a folded filter and 50 c.c. of the filtrate are transferred into an Erlenmeyer flask holding 150 c.c. A rod of chemically pure zinc 1 c.m. in length and weighing about 1½ grms. is then introduced, and 25 c.c. of chemically pure hydrochloric acid of specific gravity 1.125. The flask is then closed with a plug of wadding pressed moderately firmly, the lower end of which projecting into the flask has been moistened uniformly with basic lead acetate.

Examination of the Degree of Oxidation of Linseed Oil Varnish.—W. Fahrion (*Zeit. für Angew. Chemie*).—The author founds his process on the insolubility in petroleum ether of the oxy-fatty acids formed on the oxidation of the non-saturated fatty acids.

The Secondary Alkaloids of Belladonna.—E. Merck (*Merck's Jahresbericht*).—The author shows the

identity of atropamine and apatropine. An alkaloid obtained by Ladenburg and Roth from Gehe and Co.'s crude belladonnine, and boiling at 242° , as merely pseudo-tropine.

Determination of Total Bases in Cinchona Barks.—W. Haubensaek (*Schweiz. Wochenschrift für Pharm.*).—The author uses known processes.

Detection and Determination of Hydrochloric Acid in the Gastric Juice.—E. Salkowski, M. Rosenheim, M. Hoffmann, and others.—For this paper we must refer to the original, as also for the following papers on the "Quantitative Determination of the Phenols of Human Urine with Bromine" (Th. Rumpf); the "Detection of Hæmatoporphyrine in Urine" (O. Hammarsten); and the "Detection of Peptone" (R. von Jaksch).

Chemico-Legal Detection of Blood.—G. Janacek.—From a special memoir by the author entitled "The Limits of the Demonstrative Power of the Spectrum of Hæmatine and of the Hæmatine Crystals (Teichmann's Crystals) for the Presence of Blood: a Contribution to the Prevention of Judicial Murders." Read before the South-Slavonic Academy of Sciences and Arts, Nov. 7, 1891. Agram: Fr. Suppan, University publisher. The author recommends the spectroscopic investigation for the hæmatine of Stokes, especially since E. Hoffmann has shown its applicability not only to hæmatine but also to oxyhæmoglobine. The object in question is treated with a concentrated solution of potassium cyanide, and the solution thus obtained is examined with the spectroscope. If the cyanide is allowed to act for a sufficient time we see in the spectrum either a distinct broad band in the green, which is very similar to the band of reduced hæmoglobine, or merely a clouding of this part of the spectrum. If we add to the solution a drop or two drops of ammonium sulphide we see the band at once resolved into two bands, which at first sight resemble the bands of oxyhæmoglobine, but may be distinguished by their origin and their position, which is nearer the violet end of the spectrum. Janacek confirms the utility of this method even for the examination of the minutest objects. Thus the blood from bugs and fleas, and also the excrements of these vermin, display not merely the blood spectrum in question but Teichmann's hæmine crystals. The spectrum of hæmatine and of reduced hæmatine can be obtained intensely from the excreta of the house fly, and even hæmine crystals may be easily obtained from even the smallest quantity of fly-dirt; on evaporation the Teichmann crystals may be formed and the absorption spectrum may be obtained.

The Atomic Weight of Rhodium.—K. Seubert and K. Kobbe.—The average result is $R=102.718$, or if reduced for a vacuum $=102.652$.

Determination of the Atomic Weight of Nickel and Cobalt.—Ch. Winkler (*Berichte der Deutsch. Chem. Gesell.*).—The cause of this communication is due to the memoir by G. Krüss and F. W. Schmidt on a "New Element accompanying Nickel and Cobalt."

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 9.

The Council has adopted a new arrangement concerning "sealed papers." They will be addressed to the President, who will present them at the following meeting, mention of the fact being made in the "Proceedings." The paper will then be delivered to the keeper of the archives, who will give for each a receipt bearing the date of the day when it was received by the President.

On Acid Pyrocatechine Antimonite.—H. Causse.—Already noticed.

Specific Gravity of Textile Fibres.—Leo Vignon.—Already noticed.

On a New Ptomaine.—Dr. A. B. Griffiths.—Already noticed.

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THE

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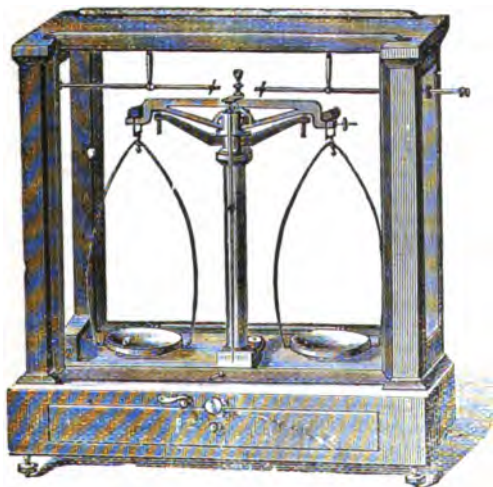


FIG. 3A

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VOL. LXVI., No. 1704.

ON AN OBSTACLE TO SCIENTIFIC PROGRESS.

By Dr. G. GORE, F.R.S.

THE recent recovery of Mr. Waterston's paper from the *Archives* of the Royal Society by Lord Rayleigh, and its publication after having lain there about fifty years (see CHEM. NEWS, vol. lv., p. 219), illustrates the less encouragement given in this country to scientific researches containing really original conclusions or phenomena than to any other kinds of such researches.

As scientific researches which are reliable and original are as necessary and valuable as those which consist of accurate measurements without originality, it seems desirable that some arrangement should, if practicable, be made, by means of which such papers as that of Mr. Waterston's (and probably others) would be saved from oblivion, and be, if possible, as competently examined and as fully recognised and published as less original ones. However important a high degree of accuracy of measurement of known phenomena is, the discovery of entirely new phenomena and new truths is essentially more important, for if no new phenomena or truths were discovered, there would be none to be measured. Out of Faraday's simple qualitative discovery of magneto-optic action arose Clerk Maxwell's mathematical theory of light.

A great obstacle, however, to the accomplishment of this very desirable object arises from the following circumstances:—(1) All new truths require to be expressed in new language; (2) In consequence of the fixity of strongly impressed previous ideas in the brain, new discoveries and conclusions are only fully appreciated by a new generation of men; and (3), As the examiners of scientific researches are frequently teachers of long experience, their ideas are apt to become so fixed by long-continued teaching that, notwithstanding their anxiety to do justice to the authors, they are unable to fully understand the new phraseology and phenomena, and therefore discourage the publication of really original researches. The so-called "conspiracy of silence" of scientific men respecting the reality of new scientific discoveries is simply a result of this fixedness of mental impression; the examiners being men of high ability and integrity hesitate to express opinions of matters which they do not fully and clearly comprehend, and other men of science follow their example and remain silent.

It is largely in consequence of this hindrance, and of the almost universal desire of mankind for some *immediate* advantage, that any and every kind of scientific occupation is more encouraged than fundamental original experiment; accounts of inventions and technical investigations are accepted and published as if they were of greater value than the discoveries upon which they are based, and accurate measurements of known phenomena are treated as if they were of more importance than the discovery of new fundamental truths; and the readiness of acceptance and publication of a new truth is often inversely proportionate to its degree of essential importance.

To make laborious and expensive researches, and have them (and especially the valuable experimental evidence contained in them) practically suppressed and consigned to oblivion simply because they are original and cannot be readily understood, is most discouraging and unjust to investigators, a great obstacle to scientific and national progress, and deserves the serious consideration of those publishing bodies who undertake the acceptance or rejection of scientific papers.

Probably the most effectual method of overcoming the difficulty would be for a committee of paid examiners, to actually repeat a sufficient number of the experiments, &c., to enable them to arrive at a demonstrable conclusion in each case. This, however, would be an expensive plan, but it would be only a small expense in comparison with that of making the researches themselves, and the importance of the object would justify the cost. The skill and labour required would be too great for unpaid examiners.

The progress of science can never be very satisfactory in this country until this obstacle is removed, nor until scientific men generally treat different problems and truths of science more in accordance with their essential degrees of importance and less according to their extrinsic or *immediate* practical value. Nor will science itself be treated with the highest respect whilst scientific men in general pursue money and trading in knowledge so much more earnestly than knowledge itself. We are all apt to be blinded by the prospect of immediate personal gain, and fail to perceive the deep-seated sources of greater good which lie latent in increased fundamental knowledge. The idea that immediate personal gain is always the greatest good, and that money is essentially more valuable and a greater source of happiness than knowledge, are only worthy of the darker ages; the greater good, however, takes a longer time to grow. Great good *must* come from new truth, even when we cannot see the way; new facts are the origin of human progress, and great truths are the parents of great uses; there can be no inventions without the facts upon which to base them, and the progress of mankind is greater in proportion as the facts discovered are more comprehensive; for instance, out of the simple qualitative fundamental fact of magneto-electric induction has arisen the dynamo-electric machine and all its world-wide uses. Other similar examples might easily be adduced.

RESEARCH NOTES FROM THE LABORATORY OF MESSRS. CROSS AND BEVAN.

The Production of Acetic Acid from Cellulose and Other Carbohydrates. By J. F. V. ISAAC, B.A. (OXON.).

ACETIC acid has been frequently identified as a product of resolution by various agencies of the carbohydrates of lower molecular weight, and its relationship to the parent molecule is in many cases easily traced. Cross and Bevan have obtained this acid as a product of the action of sulphuric acid upon the jute fibre (*Chem. Soc. Jour.*, lv., 210), and from cellulose (cotton) by fusion with alkali hydrates, the percentage yield in the latter case being under certain conditions considerable (CHEMICAL NEWS, lxx., 78). At their suggestion I have undertaken an investigation of this point not merely as empirically of interest, but as affording information of general theoretical value. I take this opportunity of noting the general scheme of the research, with typical results from amongst those already obtained.

"Fusion" of cellulosic substances with alkaline hydrates has been exhaustively studied from the point of view of the production of oxalic acid; and an elaborate paper by W. Thorn (*Dingler's Journ.*, ccx., 25), gives all the necessary data concerning the decomposition of the celluloses in this particular direction.

The production of acetic acid by the method of destructive distillation has also been largely studied, and quite recently by Chorley and Ramsay (*Journ. Soc. Chem. Ind.*, 1892, 395). The important point elucidated by these observers is the occurrence of a specific and exothermic resolution of the compounds of the cellulosic group; of this decomposition, which takes place at about 300°, the acetic acid appears to be a product. It should be noted that Thorn (*loc. cit.*, p. 27), observed the phenomenon also, but under the conditions of fusion with

alkalis, and under this condition at a lower temperature, viz., 180°.

In my investigations the results obtained by the above observers are taken more particularly into account. I confine myself to the decompositions determined by alkaline hydrates at the limits of temperature, 120°—150° and 250°—350°.

As typical members of the cellulose group I have taken cotton cellulose and the "hydracellulose" obtained from the former by the action of hydrochloric acid, and of the lignocelluloses jute and pine-wood. As a compound of more definite constitution to serve as a standard of comparison I have taken cane sugar.

The following factors of the decomposition in addition to temperature as noted above have been investigated:—

- (1) The nature of the alkali, NaOH, KOH, Ba(OH)₂;
- (2) Relative masses of carbohydrate and alkali;
- (3) Additions to the mixture of oxidising agents (e.g., K₂FeCy₆, Fe₂O₃, MnO₂) and reducing agents.

The acetic acid produced has been separated by distillation and determined by titration; checking the results by examining for the presence of other volatile acids and confirming in certain cases by conversion of the acid into silver salt and analysis of the latter.

The numbers obtained for the yields of acetic acid vary from 7 to 40 per cent of the weight of the carbohydrate; the results with the cellulose compounds are similar to those with the cane sugar. There is a considerable production of acetic acid at the lower temperature (125° to 150°), increasing with the duration of the action and also increased, *ceteris paribus*, with the addition of mild oxidising agents: the production of acetic acid of oxalic acid is greater with KOH than with NaOH. A considerable production of acetic acid has also been found to occur in certain industrial processes where vegetable fibrous materials are boiled with dilute alkaline solutions (1 to 2 per cent Na₂O) at temperatures not exceeding 110° C.

Under the conditions of my experiments there is, as is well known, a considerable evolution of gas. This will be examined for CO and CH₄ in addition to H.

These researches as far as they have proceeded lead to the following conclusions:—(1) The complex carbohydrates (saccharocolloids) break down ultimately under the action of alkalis at high temperatures similarly to those of lower molecular weight: acetic acid is a main product of the decomposition; (2) The formation of acetic acid at low temperatures indicates the presence of a CO—CH₃ grouping as equally characteristic of the former as of the latter, and from the maximum yields obtained it would appear that it is rather a simple product of resolution than of drastic oxidation, e.g., of alcoholic groups, CHOH and CH₂OH; (3) Observations upon bodies of known composition indicate that this resolution of the celluloses by the alkalis is preceded by the formation of lactic derivatives. The research is in progress, and detailed communications will be submitted in due course.

A Reaction of the Lignocelluloses and the Theory of Dyeing.

The solution obtained by adding potassium ferricyanide to ferric chloride is known to react with many "organic" compounds, prussian blue being formed as the result of the partial de-oxidation of the ferric salt (Watts' "Dictionary of Chemistry," ii., 149). The behaviour of the jute fibre in this solution is remarkable. From dilute solutions the fibre withdraws the ferric ferricyanide, which they may be assumed to contain, exhaustively: increasing in weight in proportion (we have observed a gain in weight as high as 80 per cent), and at the same time converting the compound into a "prussian blue." Analysis of the fibre so dyed show a somewhat variable ratio of Fe:CN, the mean ratio being Fe₄(CN)₁₁. Microscopic analysis shows a homogeneous union of fibre substance and colouring-matter, of which the compound may be said to represent a "solid solution." The reaction does not depend primarily upon a de-oxidation of

the ferric ferricyanide by the fibre substance, for the result is not affected by the presence of other oxidising agents, and both ferric chloride and potassium ferricyanide are only very slowly de-oxidised by the fibre substance in slightly acid or neutral solution. The combination with the ferric ferricyanide we regard as the primary result, and its conversion into prussian blue as the result of a re-distribution of its constituents through the action of the fibre constituent.

The evidence for this view, in addition to the negative points above mentioned, lies in the behaviour of the solution towards other colloids. Gelatin we find gives a greenish coagulum with the ferric ferricyanide, increasing in weight by 20—30 per cent, the reaction being constant as regards increase of weight, and also the quantity of gelatin required to precipitate a given weight of the ferric compound under constant conditions. In this case we have a simple case of interaction between two colloids in solution, the cause lying presumably in the province of solution phenomena, and there is no de-oxidation of the ferric compound.

The phenomena observed in the interaction of the jute fibre substance and that solution we divide, therefore, into the two stages—(1) combination of the two colloids by a species of "coagulation" or mutual "solid solution"; (2) a re-distribution of the constituents of the ferric ferricyanide by a more intimate interaction, within the molecule, with those of the fibre substance.

The latter phenomenon is due to the presence of OH groups of variable functions, which the further investigation of these fibre compounds is bringing more into evidence, such variation as might be inferred from proximity to CO or to CH₂ groups respectively.

In this connection we may cite the results of the researches of L. Vignon on the "Theory of Dyeing" (*Comptes Rendus*, cxii., 623), leading to the conclusion that dyeing depends on the presence of basic and acidic functions in the colouring matter and its absorbent.

We are prosecuting our investigation of these reactions with a view to the further elucidation of the mechanism of dyeing operations, as well as of the constitution of the lignocelluloses.

Determination of Molecular Weights of Cellulose Derivatives (Esters) by the Freezing-Point Method.

Mr. A. Pears, jun., has made a number of observations of the depression of freezing-point of acetic acid determined by solution of compounds of cellulose with acid radicles, e.g., acetates, nitrates, and benzoates. The observations were carried out in a Beckmann apparatus, and with careful attention to the working details prescribed by this observer.

The coefficient of depression was found in all cases unusually high, and was also observed to vary during a succession of observations with the same material.

The solution of these derivatives in acetic acid would appear, therefore, to be attended with dissociation of some kind; we have certainly been forced to the conclusion that the method is inapplicable to these solutions for the purpose of arriving at an approximation to the molecular weights of the derivatives in question.

4, New Court, London, W.C.
July 10, 1892.

ON A

NEW BACILLUS FOUND IN RAIN-WATER.

By Dr. A. B. GRIFFITHS.

I HAVE detected a new bacillus in rain-water preserved during a mild winter in a barrel exposed to the air (a time when most of the other microbia of water are inactive, and when, consequently, there prevails among them little or no struggle for existence). It is probable that the bacillus of which I am about to speak is derived from the

air, but I have not been able to find it in the atmosphere. The bacteriological examination of the rain-water in which this organism was found gave, in winter, per c.c., 32 bacteria; in spring, 292; in summer, 644; and in autumn, 665.

This species was seen for the first time in 1890, mixed with other microbia developed upon gelatin plates, sown with rain-water diluted with sterilised water; 4 c.c. of this water were diffused in gelatin liquefied at a low temperature and cultivated on plates.

The plate cultures were characteristic. In four days there is formed a small yellow colony, the circumference of which becomes yellowish, turbid, and surrounded with a zone of liquefaction. These colonies vary from 2 m.m. to 1 c.m. in diameter. In a plunge-culture in a gelatin tube the development is no less characteristic. At first from thirty-six to forty-eight hours after inoculation there is formed in the channel of the plunge a slender yellowish band whence there issue in a perpendicular direction numerous straight filaments, especially developed in the upper part, which gives the culture a downy appearance; these filaments increase by degrees, and after four days the gelatin is liquefied progressively. On the surface of the gelatin there appears a brilliant yellow colony.

In broth at 30° this species gives a yellowish scum on the surface, succeeded by a flocculent deposit of the same colour. Upon potato the culture, which grows rapidly, takes an orange colour and slowly converts the starch into glucose. The colouring-matter is insoluble in water, soluble with a yellow colour in alcohol. It dissolves also in benzene, chloroform, ether, and carbon disulphide. It has not been obtained in a sufficient quantity for study. This microbe is a true bacillus; its elements, moderately mobile, vary in length from 2 to 4 μ and in width from 0.6 to 0.8 μ . It does not form spores. It is easily stained with aniline colours, and remains coloured when submitted to the process of Gram or of Weigert. Although discovered in water, this microbe cannot live in distilled water; it requires a certain quantity of organic matter.

The vitality of the cultures resists desiccation, but not heat; a temperature of 100° kills the bacilli in fifteen minutes.

The species does not appear to have any pathogenous action. If pure cultures of this microbe are cultivated for some days upon peptonised gelatin a ptomaine is produced. It is a white solid, crystallising in nacreous needles or in klinorhombic prisms, slightly neutral to test-papers, soluble in 80 parts of water at 17°, very soluble in boiling water, moderately soluble in strong alcohol and chloroform, but not in ether.

The analysis of this formula leads to the formula $C_9H_{21}N_2O_5$. This ptomaine gives a white precipitate with sodium phosphomolybdate, a maroon precipitate with Nessler's reagent, and a yellow with tannic acid. It forms a chloraurate, a chloroplatinate, and a hydrochlorate, all crystalline. It is not appreciably poisonous, but it acts as a powerful pluretic. The author gives this bacillus the name of *B. pluviatilis*.—*Bull. de la Soc. Chim. de Paris*.

ON THE TINCTORIAL PROPERTIES OF AMETHYLCAMPHONITROKETONE AND ITS AUXOCHROMIC GROUPING.

By P. CAZENEUVE.

AMETHYLCAMPHONITROKETONE has a golden yellow colour and possesses tinctorial properties. It dyes wool and silk without mordant in a solution in dilute alcohol. If boiled with common water it decomposes the calcium carbonate of the water, giving a solution of the colour of the alkaline bichromates, and thus dyes wool and silk at the heat of ebullition. In presence of tartaric acid it dyes evenly, but it does not dye in an alkaline bath.

Cotton is not dyed directly, but when once mordanted with tannin it fixes nitroketone.

These facts are interesting in view of the present theories on the fixation of colouring matters upon animal and vegetable fibres. O. R. Witt, in particular, has established a relation between the chemical properties of substances, their colours, and their tinctorial properties. The colourless cyclical hydrocarbons, by fixing certain groups, such as NO_2 , $N=N$, $O-O$, $N-NH$, which the author calls chromophores, become chromogenes; that is to say, substances which are able to form colouring-matters. The subsequent addition of the salifiable groups OH and NH_2 , CO_2H , SO_3H , produces exactly this property of colouring or dyeing, whilst at the same time the colouration of the substance itself becomes more intense. O. N. Witt calls these groups auxochromes.

Amethylcamphonitroketone, which is of a fine golden yellow colour, is a true tinctorial substance; it certainly contains the chromophore NO_2 , but it does not seem to possess the salifiable groups which we have enumerated, and which alone are known hitherto. It departs in several respects from the nitrophenols. Its reactions are readily explained by the presence of an acid CH_2 , by the propinquity of a NO_2 and a CO . We are compelled to admit that this salifiable group, CH_2 , in virtue of its position between NO_2 and CO , gives this ketone its tinctorial properties.

This fact, without being in contradiction with the chemical theory of dyeing, shows at least that the salifiable groups OH and NH_2 , CO_2H , SO_3H are not the only ones which can give colouring properties to a coloured body. Without doubt other instances may be found among the hydrides of the cyclical nuclei.—*Bulletin de la Société Chimique de Paris*.

ON THE INFLUENCE OF THE TEMPERATURE OF COLOURED SOLUTIONS UPON THEIR ABSORPTION-SPECTRA.*

By Dr. H. BREMER.

(Concluded from p. 7).

In order to heat the solutions to the experimental temperature, 100 c.c. of the liquid were heated as quickly as possible in a flask on the water-bath a little higher than the desired temperature, making up the solvent as it evaporates. The absorption vessel, which has been heated in the meantime, is quickly rinsed out several times with the solution and filled. It is then observed by means of a thermometer warmed almost to the temperature of the liquid until the solution has cooled down to the desired point, which is then at once determined. As colouring-matters are often separated out from their solutions by repeated heating, and as more intense chemical decompositions are often effected, the liquid is always renewed after one determination.

H. Bremer carried out the examination of the coloured solutions in the first place qualitatively, examining the position of the absorptions in the spectrum by means of the universal spectroscope. If a solution has in the absorption-spectrum no bands, but merely one-sided absorptions, the instrument was adjusted with the thread-cross to their margin, and the position of the boundary of the absorption was read off on the drum of the telescope. On adjusting to the limit of absorption the intersection point of the thread-cross was adapted to the point from which no longer a distinct tone of colour was perceptible towards the stronger absorption. Ten adjustments were always made to this point, and their mean was entered in the tables.

* Being Part II. of "Contributions to Quantitative Spectra Analysis," in the *Zeitschrift für Anorganische Chemie*, No. 3.

If bands were present in the absorption-spectrum in question, the maximum darknesses of these bands were aimed at, whilst the solution was gradually diluted in the manner described by G. Krüss (*Zeitsch. Phys. Chem.*, ii., 314). Only in the case of the measurement of well-defined lines the mean of fewer than ten single determinations was taken as the result of observation. For carrying out these qualitative experiments in determining the maximum absorption of the bands, or in ascertaining the boundaries of the absorption, each substance was always examined at the same degree of concentration of its solution, but at different temperatures.

Such qualitative determinations were necessary for properly following up the quantitative determinations of the absorption of light. There appeared in the first place the following results, obtained by examining solutions both of organic and inorganic substances.

On a change of the temperature of a coloured solution there occur in *all cases* displacements of the absorptions in the spectrum. If we wish to determine exactly the position of an absorption band by measuring its maximum darkness, we should always append a mention of the temperature at which the determination was effected. It is most advantageous to work at the mean dwelling-room temperature of 17.5° , taking care the temperature of the liquid (or of the room) does not vary from this mean by more than a few degrees. In cases of fluctuations of the temperature of the liquid in question of about 6 degrees, qualitative measurements of the absorption-spectra can be effected, the results of which agree sufficiently. It is not admissible to use the solution of a colouring-matter which has had to be dissolved by the aid of heat direct for determination in its hot state without taking its temperature into account.

This dependence of the absorption relations of coloured solutions in the spectrum (certainly determined in all cases) upon temperature must have a distinct influence upon quantitative spectro-analytical determination. Such an influence must make itself felt, because in these determinations we have always, by means of the slit of the eye-piece, to cut out a perfectly definite band of the field of view of the observing telescope (*i.e.*, out of the spectrum), and in this region we must find other conditions of absorption if, owing to a change of temperature of the liquid in question, the absorption is displaced in the spectrum. In this case different parts of the absorption curve of the substance under examination will fall within the limited region at varying temperatures.

The author gives elaborate tables showing the position of the maximum darkness in the spectra of a number of solutions at given temperatures, varying in some cases from 20° to 80° .

Striking examples are contained in the above tables as shown in the determinations for tetraiodfluoresceine potassium and eosine potassium. The maximum darkness of tetraiodfluoresceine potassium dissolved in water lies between the two regions used for quantitative determinations, namely, about $\lambda 525.0$, and travels towards the red if the solution is heated. In correspondence the residual strength of light increases on warming in the region $\lambda 501.6$ to $\lambda 493.6$, whilst in the region on the other side of the band $\lambda 552.6$ to $\lambda 540.6$, the value of the strength of light falls. In like manner, in eosine potassium the regions $\lambda 508.3$ to $\lambda 501.0$ and $\lambda 528.3$ to $\lambda 521.1$, display an antagonistic behaviour, as the maximum darkness of a band lies between both regions at $\lambda 515.9$.

Besides, the intensity of the absorption in the spectra of almost all bodies varies on heating. We may measure this by leaving the position of the eye-piece slit in the telescope unaltered, but displacing the telescope so far and in the same direction as the position of the absorption is displaced qualitatively in the spectrum on heating the liquid. As an example for this case we may take the two last measurements of eosine potassium in the regions $\lambda 516.9$ to $\lambda 509.8$ and $\lambda 518.0$ to $\lambda 510.9$.

From the above measurements it appears that the tem-

perature of the light-absorbing liquid must be attended to with greater care than heretofore, not only in qualitative but also in quantitative measurements of absorption-spectra. The liquid must not during the observation be heated much more than 5° by radiant heat from the source of light. Otherwise a new specimen of the liquid under examination must be placed in the absorption cell.

If the experimentalist has not the electric light at disposal, and is not willing to introduce between the absorbent vessel and the lamp an isolating stratum for cutting off heat rays, he will do well to select a light which is not too hot, and to make use of the spectrophotometric procedure which gives the highest spectrum, *i.e.*, Vierordt's method.

NOTE ON THE RECENT DISCOVERY OF A NEW SILVER ORE.

By H. N. WARREN, Research Analyst.

THE locality known as Broken Hill in Australia has to all interested in mining operations been recognised from an early period as a vast silver region, and the author has on numerous occasions had attention directed to such minerals as fahlers, polybasite, horn silver, &c., derived from the above locality, and which from assay of the same have proved themselves valuable metallurgical products. Besides these argentiferous formations there is, however, situated in the same locality immense argillaceous deposits, consisting for the most part of ordinary kaolin.

These deposits have for years been regarded as a waste product on account of the numerous hard particles of horny substance disseminated throughout its structure, thus rendering it unfit for porcelain or other manufacture. The mass of kaolin, as far as can be ascertained, thus remained untouched until the commencement of the present year, when it was again overhauled by some travelling mineralogists, who on applying a few physical tests such as ascertaining the hardness of the particles, &c., at once became struck with their appearance and resemblance to horn silver, and being thus induced to proceed to practical tests, in so doing verifying their supposed theory, the common kaolin deposits at once foreshadow one of the richest silver harvests yet to be gleaned.

I have assayed quite recently a number of samples since the discovery of the same, and find in some the existence of silver iodide only, in others chloride only, whilst in further specimens the existence of both chloride, bromide, and iodide,—the percentage of silver averaging from 7 to 10 per cent, with traces of gold; whilst in other cases samples weighing upwards of 20 lbs. in weight of pure chloride have been obtained.

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THE SEPARATION OF SALICYLIC ACID FROM BENZOIC ACID.

By MISS J. SCHAAP.

THERE does not at present exist a good quantitative process for the separation of these acids, and hoping to effect this I first tried the precipitation with alum. I found, however, that the aluminium benzoate is not quite insoluble in water, so the method is therefore valueless for quantitative purposes. Better results were obtained by the following method.

A few mixtures, each consisting of 0.25 gm. of salicylic and 0.25 gm. of benzoic acid, were dissolved in a sufficiency of hot water and the liquids were then allowed to

cool. The salicylic acid was now precipitated by excess of bromine water, but the question had to be decided whether it was precipitated as the mono-, di-, or tri-bromo compound. I therefore took 0.25 grm. of the bromo-salicylic acid and estimated the bromine by Fresenius's lime method. The nitric acid used was free from chlorine, but the lime was not, so a check had to be made. Allowing for the small quantity of chlorine in the lime, the results in four experiments were, respectively:—0.305, 0.315, 0.319, and 0.314 grm. of AgBr. Theory requires 0.215 grm. for the mono-compound, 0.316 grm. for the di-compound, and 0.374 for the tri-compound; so it follows that the precipitate consisted of the di-compound.

Another question now arose whether the precipitate was sufficiently insoluble in water, and also whether the precipitation was complete. To solve this question 0.25 grm. of salicylic acid was dissolved in water and precipitated with bromine water. Having found that the bromo-compound is very readily soluble in chloroform, I concentrated the filtrate at a temperature of 30° and agitated the liquid with chloroform, which on evaporation did not yield the smallest residue, showing that all the salicylic acid had been precipitated. The precipitated dibromo-salicylic acids were dried in a desiccator and afterwards weighed. The weights were respectively:—0.56, 0.556, 0.551, and 0.553 grm., theory requiring 0.536 grm.

In order to directly estimate the benzoic acid, the filtrates were rendered faintly alkaline with sodium carbonate, and evaporated to a small bulk on the water, bath to expel the excess of bromine. The residues were then put into separatory funnels, acidified with hydrochloric acid, and shaken out with chloroform. This was filtered through a dry filter and allowed to spontaneously evaporate in weighed glass dishes. The results were respectively:—0.272, 0.261, 0.237, and 0.232 grm. of benzoic acid instead of 0.250 grm.—*Ned. Tydschr. v. Pharmacie, &c.*, July, 1892.

METHODS OF SUGAR ANALYSIS.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

By the term "sugar analysis" it is understood that the analysis of all the common saccharine substances, viz., sugar, molasses, syrup, starch, sugar, and honey, are embraced. In the following directions an attempt will be made to indicate the general principles which should guide the practice of sugar analysis, together with sufficient detail to enable these analyses to be carried out with accuracy and uniformity.

The principal components to be determined in the substances mentioned above are:—

- | | |
|------------------------|------------------|
| 1. Water. | 5. Sucrose. |
| 2. Ash. | 6. Lactose. |
| 3. Nitrogenous bodies. | 7. Starch sugar. |
| 4. Reducing sugar. | 8. Raffinose. |

Water.

In Sugar or Molada.—Weigh from 2 to 5 grms. into a flat dish (nickel or platinum) and dry at temperature of boiling water for three hours; cool in desiccator and weigh; return to oven and dry for one hour. If on weighing there is only a slight change of weight, the process may be considered finished; otherwise the drying must be continued until the loss of water in one hour is not greater than 0.20 per cent.

In Honey or Molasses.—(a). Proceed as above, using only 1 to 2 grms. of substance.

(b). Place 2 to 3 grms. of substance in a flat dish holding from 30 to 50 c.c.; dissolve in 70 per cent alcohol, using a small stirring-rod, which is weighed with the dish. Add from weighing bottle 15 to 25 grms. pure dry sand;

dry in oven at 70° to 80° C. until alcohol is nearly driven off; moisten thoroughly with 99 per cent to absolute alcohol; dry at 75° C. for thirty minutes, then at temperature of boiling water for an hour; repeat as above, deduct weight of added sand, and make usual calculations.

Ash.

a. Take 5 to 10 grms. of the material (sugar, molasses, honey) in platinum dish* of 50 to 100 c.c. capacity, heat at 100° C. until water is expelled, and then slowly until intumescence ceases. The dish is then placed in muffle and heated at low redness until a white ash is obtained.

b. *Soluble Ash.*—Digest ash with water, filter on to Gooch crucible, wash with hot water, dry residue at 100° C., and weigh. Difference of weights equals soluble ash.

c. Use 50 m. grms. zinc oxide to 25 grms. molasses or 50 grms. sugar. Incorporate thoroughly by adding dilute alcohol and mixing, dry, and ignite as above. Deduct weight of zinc used from weight of ash.

d. Carbonise the mass at a low heat, dissolve soluble salts with hot water, burn residual mass as above, add the solution of soluble salts, and evaporate to dryness at 100° C.; ignite gently, cool in desiccator, and weigh.

e. Saturate sample with H₂SO₄, dry, ignite gently, then burn in muffle at low redness.

f. Dissolve 10 grms. of sugar in hot water and filter to remove sand, &c.; evaporate filtrate and washings to dryness; carefully carbonise and extract with hot water until there is no longer any reaction for chlorine. Dry and ignite residue; weigh as insoluble ash. Add the soluble portion, treat with HCl in slight excess, and evaporate to dryness. Heat until all free HCl is driven off; take up with H₂O and a little HCl, filter, and wash. The residue is silica. Add NH₄OH, to filtrate, boil and filter, wash residue, which is iron and alumina. To filtrate add (NH₄)₂C₂O₄, evaporate to dryness; ignite and moisten with (NH₄)₂CO₃ and re-ignite; dissolve in water, filter, and wash. Residue equals carbonates of Ca and Mg. Evaporate filtrate to small bulk, add (NH₄)₂CO₃, and evaporate to dryness; drive off excess of ammonia cautiously and weigh. This gives the alkalies as carbonates, and this weight added to the insoluble ash, formerly determined, gives the total carbonate ash.

Nitrogenous Bodies.

Any of the methods adopted by the Association for the estimation of nitrogen may be used.

Reducing Sugar.

Reagent, Alkaline Copper Solution. (Fehling, Violette).

- | |
|--|
| 34.64 grms. pure crystallised copper sulphate. |
| 187.00 grms. tartrate soda and potash. |
| 78.00 grms. caustic soda. |

Dissolve the CuSO₄ + 5H₂O and make up to 1000 c.c. at the average temperature at which the analyses are made. Mix the solutions of Rochelle salts and caustic soda and make up to 1000 c.c. In practice use equal volumes of each reagent.

Processes (Volumetric).—a. The solution to be examined should contain about 1 per cent of reducing sugar. To 10 c.c. of the copper solution and 10 c.c. of the alkali, in a large test tube, add 20 c.c. of water, and boil. Add the sugar solution in approximately the proper quantity to reduce the copper, and boil for exactly two minutes. If, on standing for a moment, the solution is still blue, add more sugar solution and re-boil. When no longer able to distinguish any residual copper by the eye, suck a few drops of the boiling hot liquid into an end reaction tube and test the filtrate for Cu with ferrocyanide of potassium solution and acetic acid. If copper be still present, add the sugar solution little by little, boil, and re-test until no copper is found. Having thus determined the approxi-

* If the substance contains tin or other metal capable of uniting with platinum a dish made of some other material must be used.

mate quantity of sugar solution to be used, repeat the test twice, adding at first each time almost the entire quantity of sugar solution necessary to complete reduction.

b. Gravimetric.—Take 25 c.c. of copper solution of following composition:—

34.639 grms. $\text{CuSO}_4 + 5\text{H}_2\text{O}$ in 500 c.c. of water, add in Erlenmeyer flask 25 c.c. of alkali solution made as follows:—

173 grms. Rochelle salts } in 500 c.c. water.
51.6 grms. NaOH

Add 50 c.c. of a sugar solution of such strength as to leave a part of the copper unreduced; heat quickly to boiling point and boil for exactly two minutes; add 100 c.c. recently boiled cold distilled water. The liquid is poured at once into a filter tube made of hard glass with asbestos diaphragm (an ordinary extraction tube is well adapted for this purpose). The asbestos film should be previously moistened. Bring finally all the separated suboxide into the tube with the help of a feather brush, and wash with 300 to 400 c.c. of boiling water; afterward with 20 c.c. absolute alcohol, and finally with ether; then dry, heat to low redness to convert into oxide and to destroy any organic matter. The copper may also be weighed in the metallic state after reduction in a stream of dry hydrogen. The tube should in all cases be kept in a desiccator before weighing.

c. Gravimetric.—Reagents:—

34.639 grms. $\text{CuSO}_4 + 5\text{H}_2\text{O}$ }
125.000 grms. NaOH } in 500 c.c.
173.000 grms. Rochelle salts }

Process.—In a beaker of 250 c.c. capacity place 25 c.c. each of the reagents and 50 c.c. of water. Heat to boiling and add 25 c.c. of the solution to be tested, which should contain about 1 per cent of reducing sugar (dextrose, levulose). Boil for exactly two minutes, decant into a Gooch crucible, wash by decantation with 100 c.c. of boiling hot water, keeping the cuprous oxide in the beaker constantly covered. Place the beaker containing the cuprous oxide in place of the one receiving the wash water and dissolve the Cu_2O in a Gooch crucible in a fine stream of HNO_3 ; wash until all $\text{Cu}(\text{NO}_3)_2$ is removed. Transfer the whole of the nitrate from the beaker to a tared platinum dish, add a little H_2SO_4 , and evaporate over steam bath until all HNO_3 is expelled and the Cu is converted into CuSO_4 ; connect with battery of four gravity cells and allow electrolytic action to continue for three hours or until all the Cu is deposited. (Connect the dish with the zinc pole of the battery). Pour off the acid solution, adding water until all trace of H_2SO_4 is removed; wash with 95 per cent alcohol and finally with absolute alcohol; ignite residual alcohol, cool in desiccator, and weigh; calculate sugar reduced from weight of metallic copper by the following factors:—

1. Multiply weight of copper by 0.5698 for weight of invert sugar.

2. Multiply weight of copper by 0.5808 for weight of anhydrous dextrose.

These factors are correct only for a copper solution of above strength and reducing sugar of approximately 1 per cent strength.

Sucrose.—(Optical method, to be used when the sugar is approximately pure).

a. Dissolve 26.048 (for the Ventzke), (16.19 for the Laurent scale) grms. of sugar in water at temperature at which the polarisation is to be made, and, after clarification, make the volume up to 100 c.c. The sugar is conveniently weighed in a counterpoised nickel or German silver dish with large lip, whence it is readily washed into the flask. The solution before being filled to the mark is clarified by the addition of lead subacetate or phosphotungstic acid until no further precipitation takes place. Excess of lead should be avoided. The filtration and clarification may often be helped by adding a few drops of suspended aluminic hydrate after the lead.

The flask is filled with pure water until the lower line

of the meniscus coincides with the mark on the neck. The mouth of the flask is closed with the thumb and its contents well shaken, and poured into a folded filter; the first 15 to 20 c.c. of the filtrate are rejected. The subsequent filtrate, if not perfectly clear, is returned to the filter, and this continued until the filtrate shows no cloudiness. A 200 (100 to 500) m.m. tube is filled with the solution, placed in the polariscope, the scale of which, after neutralising the rotation produced by the sugar by turning the analytical prism or moving the quartz wedge, will give the percentage of sucrose in the sample taken. A dark solution may either be read in a 100 m.m. tube or the solution may be decolourised by shaking it with a small quantity of dry bone-black. A weak solution may be read in a tube from 300 to 500 m.m. in length.

b. Optical Method by Inversion.—For raw sugars, molasses, &c.

1. Method of Clerget.—Make up the solution as above and place 50 c.c. of the filtrate in a flask marked at 50 and 55 c.c. Fill to upper mark with strong HCl and mix well; place in hot water and heat quickly to 68°C .; keep at this temperature for exactly ten minutes; remove, cool quickly to room temperature, and polarise, noting temperature. If the sample contained originally any invert sugar the second polarisation should be made at approximately the same temperature as the first. The percentage of sucrose is then calculated by the following formula:—

$S = \text{percentage of sucrose.}$

$a = \text{first polarisation.}$

$b = \text{second polarisation (usually to the left).}$

$a + b = \text{sum of the polarisations.}$

$t = \text{temperature of observation in degrees C.}$

Then—

$$S = \frac{a + b}{144 - \frac{t}{2}}$$

When b is to the left, a and b are to be added; when b is to the right, it is to be subtracted from a .

2. Method of Lindet.—Place 50 c.c. of the filtrate as above in a flask marked at 100.5 c.c., add 5 grms. of powdered zinc (zinc dust), place in boiling water, and when at boiling point add, little by little, 5 c.c. of strongest HCl. After the acid has all been added, cool and make up to mark. Polarise in a 400 m.m. tube, or multiply the reading in a 200 m.m. tube by 2. Calculate percentage of sucrose as before.

Gravimetric Method.—Determine first any reducing sugar in sample by methods mentioned above; then invert sucrose, neutralise free acid, and re-determine the reducing sugar. Deduct the percentage of reducing sugar obtained at first, and the remainder will be reducing sugar derived from sucrose; multiply this number by 95 to obtain percentage of sucrose in sample.

Lactose (Anhydrous).

Take 20.56 grms. (16.19 sucrose) or 32.99 grms. (26.048 sucrose) dissolve, clarify if necessary, and complete volume to 100 c.c. The reading of the vernier scale of the instrument will give the true percentage of lactose. The lactose may also be determined by the alkaline copper method, 10 c.c. standard Fehling solution is equal to 0.067 grms. lactose. The weight of copper reduced multiplied by 0.7635 = lactose.

Lactose in Milk.

The reagents, apparatus, and manipulation necessary to give the most reliable results in milk-sugar estimation are as follows:—

Reagents.—1. *Basic plumbic acetate*, specific gravity 1.97. Boil a saturated solution of sugar of lead with an excess of litharge, and make it of the strength indicated above. One c.c. of this will precipitate the albumens in 50 to 60 c.c. of milk.

2. *Acid mercuric nitrate.* Dissolve mercury in double

its weight of nitric acid, specific gravity 1.42. Add to the solution an equal volume of water. One c.c. of this reagent is sufficient for the quantity of milk mentioned above. Larger quantities can be used without affecting the results of polarisation.

3. *Mercuric iodide with acetic acid.* KI, 33.2 grms; HgCl₂, 13.5 grms.; C₂H₄O₂, 20 c.c.; H₂O, 64 c.c.

Apparatus.—1. Pipettes marked at 59.5, 60, 60.5 c.c. 2. Sugar flasks marked at 102.4 c.c. 3. Filters, observation tubes, and polariscope. 4. Specific gravity spindle and cylinder. 5. Thermometers.

Manipulation.—1. The room and milk should be kept at a constant temperature. It is not important that the temperature should be of any given degree. The work can be carried on equally well at 15° C., 20° C., or 25° C. The slight variations in rotary power within the above limits will not affect the result for analytical purposes. The temperature selected should be the one which is most easily kept constant.

2. The specific gravity of the milk is determined. For general work this is done by a delicate specific gravity spindle. Where greater accuracy is required, use specific gravity flask.

3. If the specific gravity be 1.026, or nearly so, measure out 60.5 c.c. into the sugar flask. Add 1 c.c. of mercuric nitrate solution, or 30 c.c. mercuric iodide solution, and fill to 102.4 c.c. mark. The precipitated albumen occupies a volume of about 2.44 c.c. Hence the milk solution is really 100 c.c. If the specific gravity is 1.030, use 60 c.c. of milk; if specific gravity is 1.034, use 59.5 c.c. of milk.

4. Fill up to mark in 102.4 c.c. flask, shake well, filter, and polarise.

Notes.—In the above method of analysis the specific rotatory power of milk sugar is taken at 52.5, and the weight of it in 100 c.c. solution to read 100° in the cane-sugar scale at 20.51 grms. This is for instruments requiring 16.19 grms. sucrose to produce a rotation of 100 sugar degrees. It will be easy to calculate the number for milk sugar, whatever instrument is employed.

Since the quantity of milk taken is three times 20.51 grms., the polariscopic readings divided by 3 give at once the percentage of milk sugar when a 200 m.m. tube is used.

If a 400 m.m. tube is employed, divide reading by 6; if a 500 m.m. tube is used, divide by 7.5.

Since it requires but little more time, it is advisable to make the analysis in duplicate and take four readings for each tube. By following this method gross errors of observation are detected and avoided.

By using a flask graduated at 102.4 for 60 c.c. no correction for volume of precipitated casein need be made. In no case is it necessary to heat the sample before polarising.

(To be continued.)

ON NATURAL PHOSPHATES.*

By J. LAINSON WILLS, F.C.S.

(Continued from p. 29).

OCCURRENCE OF NATURAL PHOSPHATES IN THE GEOLOGICAL EPOCHS.

Post-tertiary or Quaternary System.

True guanos.
Crust or "leached" guanos.
West Indian and Pacific phosphates.

Tertiary System.

West Indian rock phosphates.
Nassau or Lahn nodular concretions.
Suffolk coprolites in the Red Crag and Coralline Crag.
(Reposing on the Lower Eocene.)
S. Carolina beds, resting upon Eocene.

* A Paper read before the Ottawa Field-Naturalists' Club.

Deposition of Florida phosphate *débris* and organic remains.

N. Carolina overlying Eocene marl.
Fundamental rock of Florida phosphate deposits.
Clays and *débris* of Bordeaux phosphates.

Cretaceous System.

Belgian (Liege) Hesbaye nodules.
American Alabama amorphous nodules.
New Jersey marls.
Belgian (Mons) Ciply nodules (Maestricht beds).
Somme deposits, arenaceous and nodules.
Russian "Samorod" nodules Desna-Don.
Cambridgeshire and Bedfordshire coprolites.
French nodules of Ardennes, Meuse.
" " Montpellier and Bellegarde.

Oolitic or Jurassic System.

Bordeaux phosphorites and nodules overlain by tertiary (eocene) clays and *débris*.
Algerian phosphates.

Triassic System.

Highly phosphatic beds (between trias and below lias) containing exuviae of huge reptiles as well as remains of fish and crustaceans.

Permian System.

(Appearance of reptilia).

Carboniferous System.

(Appearance of amphibia).

Devonian or Old Red Sandstone.

Highly phosphatic beds in conjunction with lower carboniferous.

Highly phosphatised beds in Shropshire containing oldest known remains of vertebrate life associated with crustaceans.

Silurian System.

(Appearance of vertebrata).
Welsh Bala beds. Berwyn phosphate mine.
Lingula flags (Quebec) 40 per cent tribasic.
Angers slates (France).
Phosphate limestone of Kentucky.
Logrosan (Spain) phosphorites (apatites?).
Caceres (Spain) " "
Portugal phosphorites.

Cambrian System.

(Appearance of protozoa, mollusca, annuloida, and crustacea).

Laurentian System.

Canadian apatite.
Norwegian apatite.

Thus at the present time we have mineral phosphates of lime in process of formation, and principally known in commerce as "crust guano."

Looking at the chemical composition of average bird guano, we find it to be composed of the following constituents:—

Moisture..	..	..	..	..	..	15.8
Organic matter and ammoniacal salts	..	..	..	..	..	52.5
Phosphates of lime	..	..	..	..	..	19.5
Phosphates of iron and alumina	..	..	..	..	..	3.1
Alkaline salts..	..	..	..	..	..	7.6
Silica and sand	..	..	..	..	..	1.5

This typical analysis is from the average of fifteen samples made by Nesbit on the Chinchas Inland guano.

An elementary knowledge of chemistry will assist us to perceive what a large proportion of the above constituents will be leached out by water or dissipated by prolonged exposure to ordinary atmospheric influences,

especially when we remember that the organic matter above mentioned comprises uric, oxalic, and phosphoric salts of alkalies and ammonia, and even about one-third of the phosphates of lime is found to be soluble in water. Given a deposit of guano on a limestone soil or rock, and it is readily perceived that every shower will contribute to the steady but continual process of the transmutation of the carbonate of lime into phosphate of lime in consequence of the discharge of the weaker carbonic acid by the stronger phosphoric acid.

The exhausted guano then becomes phosphatic in distinction to being nitrogenous and ammoniacal ("leached"), and the subjacent limestone undergoes a metamorphosis by a double decomposition into phosphate of lime. If the absorbing limestone is pure, the phosphate of lime formed thereby will be correspondingly pure; and on the other hand, if the calcareous base is intermixed with clay or sand or ferruginous material, the newly formed product will contain alumina, silica, oxide of iron, &c., in like proportions.

Such has been the undoubted origin of the deposits of Aruba rock phosphate, samples of which are on the table, and which are typical of this kind of metamorphosis and will serve to illustrate many similarly formed deposits, notably those of Curacao, Sombrero, Navassa, and Redonda (in which latter case the subsoil must have been aluminous, since the mineral is a phosphate of alumina).

In some cases the phosphatic principle may have been derived from animal *debris*, such as bones.

The composition of animal bones varies somewhat according to the animal furnishing them, and even with the particular part of the same animal; but the following analysis, expressed in 100 parts, may be taken as an average:—

	Green bones.	Bone ash.
Moisture	33.0 (gelatin)	
Organic matter		
Phosphate of lime	56	} 70—75 per cent.
Phosphate of magnesia	3	
Carbonate of calcium	3	
Alkaline salts	4	
Silica		

The bones of birds are even richer in phosphoric acid than those of animals, but bones of amphibia and fish contain less than those of birds and animals.

Amongst other animal organisms rich in phosphoric acid or phosphate of lime may be mentioned certain shell fish, or rather their shell remains, notably the shells of *Lingula* and *Orbicula*, which consist for the greater part of phosphate of lime, and are found in accumulated beds in the Lower Silurian rocks, being thus described by Sir Wm. Logan ("Geology of Canada," 1863).

Those coming from the Chazy formation at Alunette Island left after calcination 61 per cent of fixed residue consisting of—

Phosphate of lime	85.7
Carbonate of lime	11.7
Magnesia	2.6

100.0

and analysis of the original material gave as follows:—

	Alumette.	Hawkesbury.	R. Ouelle.
Phosphate of lime	36.38	44.70	40.34
Carbonate of lime and some fluorine	5.00	6.60	5.14
Carbonate of magnesia	—	4.76	9.70
Oxide of iron and alumina	7.02	8.60	12.62
Magnesia	—	—	—
Insoluble	49.90	27.90	25.44
Volatile by heat	1.70	5.00	2.13
	100.00	97.56	95.37

We here observe an average of 40 per cent of phosphate of lime. It would appear that our knowledge of the pro-

portion of phosphatic element in similar animal remains is very imperfect, so that upon further investigations we may expect to meet with many other similar accumulated supplies of phosphoric acid.

Some authorities attribute a large portion of the phosphate of lime in the Charleston fields to such molluscs and principally *Lingula pyramidata*, which are found abundantly on the present coast.

Classification of Natural Phosphates.

I prefer for all practical purposes and from rational observation to modify the classification proposed by Dr. Penrose, thus:—

Apatites	{ Fluor-apatites. Chlor-apatites.
Mineral and rock phosphates	{ Phosphorites. Nodules, coprolites. Concretions. Conglomerates. Phosphatic limestone. Phosphatic marls. Crust guanos.
Guanos	{ Nitrogenous. Phosphatic, or leached. Bat guano.
Animal remains	{ Bone beds. Shell beds. Animal exuviae.

We will now proceed to trace in a cursory way the commercially known deposits, commencing with the most recent and passing stratigraphically in descending order to the more ancient formations.

Guanos.

Guanos are of two kinds,—nitrogenous or those containing their original manurial qualities, and phosphatic or "leached," the latter being in a more or less mineralised condition by exposure to weathering.

Among the nitrogenous guanos we have the Peruvian, Ichaboe, Patagonian, and Falkland Islands.

The phosphatic or weathered guanos include those of the Pacific or Polynesian Islands, Sydney, Phoenix, Starbruck, Baker, Howland, Jarvis, Enderbury, Malden, Lapede, and Arbrohlos Islands.

Some of these deposits are more or less exhausted, and new islands furnishing similar products are from time to time worked.

The West Indian guanos are from Aves, Mona, Tortola. Other South American are Patos Islands, Megillones, Rata.

From Africa, Saldanta Bay and Kuria Muria Islands.

Bat guano, the product from the floors of caverns inhabited by bats, have sometimes been sent to market as a rich fertiliser. It is found notably in Cuba (W. I.) and in N. Borneo. It possesses a characteristic dark brown colour, and exhibits the undigested parts of beetles' wings and insect *debris*.

Bone Beds.

These are found in nearly all sedimentary strata from the Devonian up to the present time, but with the appearance of those remarkable reptilia in the Permian age we find that these kinds of phosphatic provisions of nature took enormous developments, augmenting the resources previously furnished by the amphibia of the carboniferous epoch.

Bone beds, however, in their original state have furnished little to commercial supplies of phosphatic products, except those found in the tertiary and quaternary ages, such as Bordeaux, Carolina, Florida, and Sombrero (breccia).

Shell Beds.

Since these must have existed from a time well into the paleozoic periods, or that is to say from the Cambrian

age, we may expect and do find these mollusca remains through a wide range of systems and strata and up to recent times.

The Silurian *Lingula* beds are remarkable, and have been already particularised as a prebable abundant source of phosphoric acid.

The Welsh Silurian beds and the French Bellegarde and Ardennes deposits in the lower Green-sand (cretaceous) exhibit evidence of this origin, while the tertiary and quaternary phosphates contain very frequently these marine and fluvatile remains as a contribution to their value in phosphate of lime.

Some very interesting specimens are on the table from the Dutch West Indies containing from 75 to 80 per cent of tribasic phosphate of lime, and exhibiting in some cases one mass of shells belonging to recent times.

Coprolites

Owe their name to Professor Henslow, and should be applied only to the fossil exuviae of animals. The appellation has extended itself to many rolled or gravelly products, chiefly found in the cretaceous formation. In England they have been worked to a large extent in Bedfordshire and Cambridgeshire, where they appear in the (Neocomian) strata, between the chalk and the sub-jacent Jurassic system, in nodules and pebbles of size from a pea to a hen's egg, and sometimes cemented by ferruginous sand into a hard conglomerate; organic remains are present, and casts and fragments of fossils with abundance of ammonites, vegetable remains, and other debris of the Jurassic epoch (*Iguanodon* and *Megalosaurus*, &c.).

The commercial products contain from 45 to 55 per cent phosphate of lime.

The coprolites of Suffolk occur in the tertiary, being in the older pliocene (the red crag and coralline crag). They are poorer in phosphate of lime, more ferruginous and harder in texture.

France also possesses some deposits of this character at Bellegarde, near the Swiss frontier, and also at Montpellier and Avignon, yielding 54 per cent tribasic phosphate of lime.

(To be continued).

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 31).

The Determination of Occluded Gases.

AFTER so much negative evidence, the only remaining hypothesis which could account for the irregularity of the atomic weight of copper deduced from cupric oxide is that of the occlusion of gases by the substance. This idea is by no means new. As long ago as 1842 Erdmann and Marchand (*Journ. fur Prakt. Chemis.*, xxvi., 461), showed that at least a small amount of air was condensed by the substance. Frankland and Armstrong (*Chem. Soc. Journ.*, xxi., 89, 93), found in 1868 that cupric oxide prepared from the nitrate contains both carbonic acid and nitrogen. Hilditch (*CHEMICAL NEWS*, xlix., 37, 1884), states that oxygen gas is occluded by cupric oxide at a red heat, and estimates the effect of this impurity upon the atomic weight of oxygen without, however, adducing any experimental data. More recently Morley (*Amer. Journ. Sci.*, xli., 231, March, 1891), has found that cupric oxide slowly gives off a gas in vacuum. It is a noticeable fact that cupric oxide is almost as serviceable as platinum in preventing bumping during ebullition.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

The simplest and surest method for the liberation of an occluded gas is completely to dissolve the cupric oxide in a pure acid. It is by no means certain that indefinite heating in a vacuum would accomplish the end in view. Several pieces of apparatus more or less suitable for the present purpose were devised in succession, and by their means it was proved that some varieties of cupric oxide occlude important quantities of æriform material. Nearly fifty determinations were made.

According to the first method a tube of the shape shown in Fig. 1 was filled at the end with freshly ignited

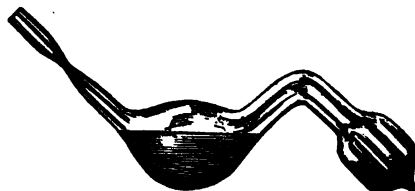


FIG. 1.

cupric oxide, and in the middle with pure boiled sulphuric acid. When the whole had been completely exhausted by means of a Sprengel pump, the liquid was allowed to come in contact with the solid, and the gas evidently set free was pumped out and measured. But the action was of course only a very superficial one, and no amount of long standing or violent shaking could accomplish a more complete change. Three experiments indicated that at least a small amount of gas, which appeared to be chiefly nitrogen, was set free. Since it was difficult to decide how much cupric oxide had been combined, the method was abandoned.

Subsequently, more dilute boiled sulphuric acid was used; and the apparatus was sealed by fusion after exhausting, but before mixing the acid and base. The mixture was digested upon the water-bath until the action was nearly or quite completed. It was found that this completion was greatly facilitated by violent shaking at the moment when the acid was poured upon the cupric oxide, for otherwise the materials inevitably formed a hard cake which dissolved very slowly. In one or two cases a small amount of unchanged cupric oxide was weighed, and subtracted from the original amount.

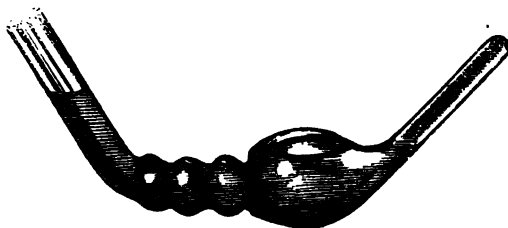


FIG. 2.

The apparent evolution of gas was at first very violent, but this violence might have been partly due to ebullition caused by the heat of the chemical action. The tubes were opened under boiled water or mercury, and the gas was analysed by means of Hempel's apparatus, somewhat modified for accurate use with very small quantities of material. The portion of the gas which was not absorbed by caustic potash, but was absorbed by pyrogallol, is tabulated below as oxygen. The remainder refused to support combustion, suffered no diminution of volume upon the addition of oxygen, and appeared perfectly inert; hence it was undoubtedly nitrogen. In order to test the solution of pyrogallol, analyses of air were made from time to time with satisfactory results. The volumes were of course corrected for temperature and pressure,

Occluded Gas in Cupric Oxide.—First Series.

No. of exptmt.	Weight of cupric oxide. Grms.	Vessel employed for ignition.	Temperature of ignition.	Vol. of gas evolved uncorr. C.c.	Vol. of O ₂ for 1 grm. CuO. C.c.	Vol. of N ₂ for 1 grm. CuO. C.c.	P.c. of gas in CuO by weight.
58	4.35	Porcelain	Dull red	2.70	0.03	0.59	0.075
59	3.12	{ Double xble Platinum	Bright red	0.30	0.01	0.09	0.012
60	Blank	—	—	0.10	—	—	—
61	1.20	—	Not ignited	3.5 of CO ₂	Trace	Trace	—
62	Blank	—	—	0.10	—	—	—
63	1.20	Porcelain	Dull red	0.73	0.03	0.58	0.073
64	2.20	"	"	1.34	0.03	0.58	0.073
65	2.00	"	"	0.8±	Trace	0.40	0.05±
66	3.20	{ Double xble Platinum	"	1.70	0.05	0.48	0.064
67	2.10	Porcelain	"	1.13	0.00	0.53	0.065

as well as for the tension of aqueous vapour, before the weights of gas were calculated. The conditions varied so little from the mean, 24° C. and 750 m.m., that a statement of these data seems inessential.

The occlusion of an inert gas by cupric oxide was so peculiar a phenomenon that many experiments were needed to carry conviction. Several blank experiments were tried in order to test the freedom of the acid from dissolved air. The fact that only a very small amount of gas was evolved in the second experiment is also valuable evidence upon this point.

The material used in experiments 58, 63, and 64 was four years old, while that used in experiments 59, 65, 66, and 67, had been recently prepared. Both of these samples were made from cupric oxynitrate, whereas the one used in experiment 61 was precipitated by caustic alkali. The tubes of Nos. 64 and 67 were opened under mercury. In No. 64 the cupric oxide was cooled for 48 hours after igniting, while in No. 66 the oxide was still very hot when introduced into the tube.

The series was discontinued because a new method had been devised which was much less tedious and much more direct in its execution. According to the new method, the cupric oxide to be analysed was introduced into a tube shaped in the manner shown in Fig. 2. After the bulbs had been nearly filled with thoroughly boiled warm water, the open mouth of the tube was connected with an air-pump to remove any mechanically adhering air. The water was usually allowed to boil for several minutes under the reduced pressure. The air was then readmitted, and the tube was entirely filled with pure boiled water, being placed perpendicularly for the purpose. When the tube had been returned to its usual position, acid was added through a fine funnel tube in such a manner that it at once attacked the oxide. A short piece of glass rod in the large bulb together with constant agitation prevented the formation of cakes.

In the most carefully performed experiments the sulphuric acid as well as the water was boiled, but repeated trials showed this precaution to be unnecessary. In one blank experiment even ordinary distilled water and sulphuric acid evolved only about one thousandth of a c.c. of gas, while boiled water, which was invariably used in the determinations, gave no trace even of the finest bubbles with unboiled sulphuric acid.

The gas evolved on the solution of the cupric oxide was collected chiefly in the largest bulb. The amount collected in the smaller bulbs decreased in proportion with the increase of distance from the first, and only a very small amount was lost through the open mouth. The gas was measured in the right hand graduated tube, or drawn off for analysis through a rubber connector attached at this end.

The apparatus was afterwards modified to avoid the slight loss through the open mouth. It then consisted of a small stoppered flask with two concentric funnel tubes, and a delivery tube closed with a rubber connector and a pinch cock. When the whole apparatus had been filled with boiled water through the larger funnel tube,

the smaller one was filled with pure sulphuric acid and quickly placed inside the larger one. Upon inclining the flask it is evident that the loss of minute bubbles must have been reduced to a minimum, while the small annular opening between the funnel tubes was quite sufficient to allow the escape of the displaced water. The gas was readily drawn off for analysis through the delivery tube, which just penetrated the smooth rubber stopper.

(To be continued).

SIXTY-FIFTH CONGRESS OF GERMAN
NATURALISTS AND PHYSICIANS.

THIS Congress, first instituted by the illustrious Oken, amidst difficulties arising from the mistaken jealousy of the German governments, now enjoys full recognition from all quarters. Its meeting will this year take place at Nürnberg from the 12th to the 16th of September. The Congress differs in several important respects from its daughter the British Association. It includes not merely "natur-forscher," i.e., men engaged in scientific pursuits, but physicians who of course are, or ought to be, men of science.

The number of sections is thirty-two:—1. Mathematics and astronomy; 2. Physics; 3. Chemistry; 4. Botany; 5. Zoology; 6. Entomology; 7. Mineralogy and geology; 8. Ethnology and anthropology; 9. Anatomy; 10. Physiology; 11. General pathology, pathological anatomy; 12. Pharmacology; 13. Pharmacy and pharmacognosis; 14. Internal medicine; 15. Surgery; 16. Obstetrics and gynaecology; 17. Pædiatry; 18. Neurology and psychiatry; 19. Ophthalmology; 20. Otiatrics; 21. Laryngology and rhinology; 22. Dermatology and syphilis; 23. Hygiene and medicinal policy; 24. Forensic medicine; 25. Medical geography, climatology, hygiene of the tropics; 26. Military sanitation; 27. Dentistry; 28. Veterinary medicine; 29. Agricultural chemistry and agricultural experiments; 30. Instruction in mathematics and natural science; 31. Geography; 32. The knowledge of instruments.

This arrangement of sections, though of course not free from objections, has one signal advantage over that of the British Association,—the absence of the section of statistics and political economy. The Germans do not need to be laboriously told that statistics must rank merely as a method, available in various sciences, but never as an independent science. Political economy, too, wherever introduced, finds an easy transit into party politics.

The Nürnberg meeting is open to foreign savants, whose participation will be welcome. The subscription for the session is 12 marks (shillings), but those only who have in addition paid a yearly subscription of 5 marks are entitled to take part in the official deliberations of the Congress and to vote for or against resolutions. Each section is opened by an introductory president appointed by the general committee and then nominates its permanent president.

On Monday, September 12, the Congress is invited by the municipal authorities to a social reunion at 8 p.m. in the Park of the Rosenau Society. The festal banquet takes place on Wednesday, September 14, in the Hotel Zum Strauss, and the festal ball on Thursday, September 15, in the same locality. On Monday, September 12, a general meeting will be held at 9 a.m., at which discourses will be delivered by Professors His, Pfeffer, and Hensen. At 3 p.m. the sections will be opened. On Tuesday, September 13, the sections sit in the morning, and at 2 p.m. the members have the choice of three excursions to Erlangen, to the stalactitic cavern of Krottensee, or to the prehistoric circular entrenchment Huberg, near Pommelsbrunn.

On Wednesday, September 14, will be a general meeting, at which papers will be communicated by Prof. Dr. von Helmholtz, Prof. Strumpel, and Prof. Ziegler, and at 5 p.m. ensues the banquet at the Hotel Zum Strauss. Thursday, September 15, will be given up to sectional work, but at 8 p.m. there will be held a ball at the Hotel Zum Strauss.

On Friday, September 16, will be held the final general meeting, when Prof. Günther will discourse on the physical and geographical phase of volcanic phenomena, and Prof. Hüppe on the ætiology of infectious diseases.

Applications for lodgings should be made as early as possible to Herr J. Gallinger (Bergstrasse 8). The number of beds, &c., required should be accurately stated, and it must be noted that attention to applications made later than August 31 cannot be guaranteed.

Applications relating to sectional business should be addressed to the respective secretaries. Other letters (excepting applications for apartments), are to be forwarded to Dr. G. Merkel, Josephsplatz 3. From the names of the *savants* announced as about to take part in the proceedings a most interesting gathering may be expected.

NOTICES OF BOOKS.

Biographical Notice of President Henry Morton, Ph.D., of the Stevens Institute of Technology. Prepared by Prof. COLEMAN SELLERS, E.D., and Prof. ALBERT R. LEEDS, Ph.D. On the Occasion of the Presentation to the Trustees and Faculty by the Alumni Association of a Portrait of President Morton, February 15, 1892.

We have here a graceful tribute paid by his colleagues and pupils to a *savant* of distinguished merit.

Dr. Henry Morton, President of the Stevens Institute of Technology, is remarkable for his versatility, but we may apply to him the old saying "*nihil tetigit quod non ornavit*." In his career as a student at the University of Pennsylvania he entered with keen interest into literary pursuits, and even took up painting, in which he reached a higher position than that of a mere *dilettante*. In a meeting of the College Philosophical Society he made the daring proposal "that a committee be appointed to translate the inscriptions on the Rosetta Stone, and present the translation to the Society at a future meeting."

This celebrated stone had been already studied by no less authorities than Young and Champollion, though no complete translation had been executed. Mr. C. R. Hale (Dean of Davenport), undertook the Greek and Demotic texts, whilst Morton himself took the hieroglyphic portion in hand. For this purpose he threw himself into the special study of hieroglyphics, and in order to reproduce the designs he acquired the art of lithography. We may here remark that the studies of archaeology, of ethnology, and all their accessory disciplines are strikingly popular in America.

After graduating he devoted himself at first to the study of law in the chambers of Mr. G. M. Wharton, of the Philadelphia bar. In 1859, however, he gave up his

legal studies and occupied himself with chemistry and physics. Here we must salute him as an able and successful reformer in higher education. The claims of natural science to a place in the curriculum of Universities not less prominent and honourable than that hitherto monopolised by "classics" or "humanities" were felt in America as early as in Europe. The Episcopal Academy of Philadelphia, one of the preparatory schools of the University, took part in this movement, and young Morton undertook to give some lectures on chemistry and physics which would be interesting to boys. The success of the undertaking went beyond all expectation. "The boys found the novel and brilliant experiments, the clear and entertaining explanations of the facts and phenomena of every day life and experience, so much more entertaining than the derivation of a Greek root, or the history of Remus and Romulus, that the little room in the course of a few weeks became too small for those who wanted to come in." A large and well equipped lecture-room was arranged for the lectures and researches of Prof. Morton. "The new lecture-room speedily became famous, and in the afternoons at extra lectures was crowded with pupils from other city academies, and in the evening with older listeners who were glad to spend a delightful hour in hearing striking expositions of the novel discoveries in physical science."

In 1863 Mr. Morton was elected Professor of Chemistry at the Philadelphia Dental College, and in 1864 he became Resident Secretary of the Franklin Institute.

Among his other successful endeavours to revivify the somewhat decaying Institute he delivered public lectures on reflection, refraction, sunlight, moonlight, eclipses, fluorescence, &c. The general American public seem to take a livelier interest in scientific lectures than is displayed in this country, but this course was rendered especially attractive by the original devices of the author for illustrating his discourses. Even professional men confessed themselves startled by the effects produced. The artificial rainbow, the combustion of a sword from hilt to point, and the illumination of an entire theatre with the monochrome yellow light, the "legions of angels," and the "artificial eclipse" were received with enthusiasm.

In 1868 Prof. Morton accepted as an interim arrangement the Chair of Chemistry and Physics at the University of Pennsylvania, during the absence of Prof. J. F. Fraser. On his return the department was divided and a new Chair of Chemistry was created and was accepted by Prof. Morton. About this time he discovered the nature of the bright line seen on the sun's disk near the edge of the moon during partial eclipses (see CHEMICAL NEWS, vol. xx., p. 313).

In 1870 Prof. Morton resigned the secretaryship of the Franklin Institute and accepted the Presidency of the Stevens Institute. In 1878 he accepted a position as Chairman of the Committee of Scientific Tests in the Lighthouses Board of the United States, vice the late Prof. Joseph Henry. He has long been recognised as the foremost scientific expert in New York in patent litigations and in similar cases. It must be remarked that in the United States, despite the careful examination instituted before granting a patent, disputes as to the validity, the proprietorship, and the scope of a patent, seem not less frequent than in Britain.

We do not know whether the attention of Prof. Morton was ever drawn to the necessity of altering the present system of taking scientific evidence, and of making the expert the assessor of the Court, instead of the witness "called" by either party and treated by the other as a kind of informal advocate.

The scientific researches of Prof. Morton have been numerous and important, and would have been largely multiplied had not so much of his time been occupied by his official duties.

Foremost must come his investigation of the fluorescent and absorbent spectra of the uranium salts. For the

details of this research the reader must be referred to the *CHEMICAL NEWS*, vol. xxviii., pp. 47, 113, 169, 233, 244, 257, and 268; and vol. xxix., p. 17. In 1872 and 1873 followed a series of investigations on the fluorescent relations of anthracene, pyrene, chrysene, and a new solid hydrocarbon (thallene) found in petroleum distillate (see *CHEMICAL NEWS*, vol. xxvi., pp. 199, 272, and vol. xxxiv. p. 188). Concerning the value and the importance of these researches we need merely mention their appreciation by Sir G. G. Stokes, of Cambridge, and by Dr. Tyndall.

Prof. Morton's attention was given to a considerable extent to the development of the magic lantern as a means of illustrating lectures. An account of his improvements will be found in the *CHEMICAL NEWS*, vol. xxix., p. 92, and vol. xxv., p. 251.

A paper which appeared in 1879 (*CHEMICAL NEWS*, vol. xxxix., p. 255), treats of "the chronology of the isomeric purpurines and the actual relations of some of the bodies which have been called anthrapurpurine, isopurpurine, and flavopurpurine." There seems good reason to conclude that he was the first to isolate and recognise flavopurpurine.

Other published researches relate to the elimination of antimony from the human system, to the measurement of incandescent lamps, and to so-called water-gas. He is one of those who eschew the error of explaining physical facts by ultra-human agencies. At the same time, as we may be pardoned for remarking, and as he shows very ably in a paper on "The True Relations of Physical Science to Religion" (Stevens's "Indicator," 1888, vol. v., p. 158), he insists that science and religion can neither directly support or refute each other.

It is interesting to note that whilst Prof. Morton is highly esteemed as an original investigator, as a lecturer, and as an educational organiser, he is no less appreciated among a wide circle of friends, among his colleagues and pupils, for his unvarying courtesy and kindness.

The illustrations of this book are beautiful, whether they display fluorescent spectra, photographic views of lunar scenery, or fanciful designs.

We hope that Prof. Morton may long survive to exert his varied talents and to promote the scientific culture of his country.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 26, June 27, 1892.

Contribution to the Study of the Function of Camphoric Acid.—A. Haller.—M. Friedel ascribes to the molecule in question the threefold function of a carboxylic acid, a ketone, and an alcohol, whilst the majority of authors who have occupied themselves with this substance consider it as a dicarboxylic acid. These differences of opinion bear merely upon the constitution of the nucleus C_8H_{12} .

On Aluminium.—M. Balland.—Towards the end of last year H. H. Lubbert and Roscher announced that aluminium was attacked by wine, brandy, coffee, and tea, and was consequently not a fit material for field flasks or other vessels of the same kind. The news propagated by the press has caused doubts as to the future of this metal, doubts which have been shared by the War Department. The author has undertaken numerous experiments to check the assertions of the German chemists. The material employed was sheet aluminium produced in France, of the quality met with in trade. It is 1 m.m. thick and weighs 2775 grms. per square decimetre.

For these trials plates were taken of 5 grms. in weight, measuring 18 square c.m., and presenting a surface very close upon 38 square c.m. These plates before being put in use were cleaned with all desirable care, as were also the vessels employed. It results from our experiments, which were pursued for some months, that aluminium may be employed with advantage in the manufacture of utensils for domestic use. Air, water, wine, beer, cider, coffee, milk, oil, butter, fat, &c., urine, saliva, soil, &c., have less action upon it than upon the common metals (iron, copper, lead, zinc, tin). Vinegar and common salt indeed attack it, but in proportions which should not interfere with its employment. It loses in vinegar in four months only 0.349 grm. per square decimetre, and 0.045 grm. in 5 per cent solutions of salt.

Action of Chlorine upon the Alcohols of the Fatty Series.—A. Brochet.—In this paper the author studies the chlorisobutylic paraldehyde a , $C_{12}H_{21}Cl_3O_3$.

On Asboline (Pyrocatechine and Homopyrocatechine).—M.M. Béhal and Desvignes.—Asboline is a substance which Braconnot obtained from the soot of wood-smoke, and which he regarded as a definite nitrogenous compound. The author has resolved it into two portions, $C_6H_6O_2$ and $C_7H_8O_2$.

On Vegetable Cholesterines.—M. Gérard.—The cholesterines extracted from phanerogamous plants have all the physical and chemical characters of Hesse's phytosterine. The cholesterines extracted from cryptogamous plants give the same reactions as Tanret's ergosterine. Tanret indicates the following differential reaction. On treating a small quantity of phytosterine with concentrated sulphuric acid, the phytosterine takes a reddish brown colour and dissolves incompletely. If chloroform is then added to the mixture the latter takes a yellow colouration, which soon turns to blood-red and to violet. Animal cholestere gives the same reaction. On the contrary, ergosterine dissolves completely in concentrated sulphuric acid, and if chloroform is added to the mixture it remains colourless. Cholestere has been extracted from the lupin, from fœnugreek, from the seed of Datura, and from olive oil. Among the lower plants the author has obtained it from *Æthaliu septicum* and *Penicillium glaucum*.

Researches on the Falsification of Essence of Santal-Wood.—E. Messard.—By using pure ordinary sulphuric acid it is easy to ascertain if an essence of santal is pure or if it is mixed with essences of cedar, cubebs, copaiba, turpentine. In the former case the reagent gives a viscid liquid which becomes a paste, and is rapidly transformed into a solid mass adhering very strongly to the glass. This mass is easy to recognise by its light grey-blue or greyish colour and the dusty aspect which it assumes with age. In the second case the resinous mass does not solidify entirely and always retains a deep colour with a very distinct lustre.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 9.

Nitroketone derived from the Camphosulphophenols.—P. Cazeneuve.—The author has examined the potassium, ammonium, calcium, barium, copper, lead, and silver derivatives of this compound, as also certain alkaloidal derivatives.

Action of Hydriodic Acid upon Carbon Tetrachloride.—B. Walfisz.—This is a case of the formation of iodoform without the presence of an alkali, and setting out from a derivative of methane.

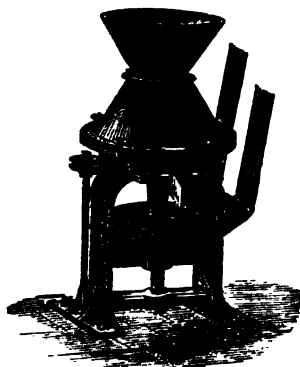
Study of the Azo- and Alkyllic Derivatives of Chrysaniine as well as of the Colouring Substances thence Derived.—A. Trillat and de Rackowski.

Decomposition of Silver Permanganate and a peculiar Association of Oxygen with Silver Oxide.—A. Gorgen.—Already noticed.

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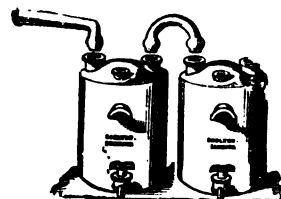
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Liquid SO₂ in Syphons, for Lectures, &c.

PHOSPHORIC ACID and PHOSPHATES.

NITRATES: Nitric Acid,
of STRONTIA, BARYTA, &c.

CARAMELS for all purposes.

A. BOAKE, ROBERTS, & CO.
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THE CHEMICAL NEWS.

VOL. LXVI., No. 1705.

THE CENTRIFUGAL EMULSOR.

By MARTIN EKENBERG.

By the aid of this machine uncongenial fluids, as for instance oil and water, may be caused to mix mechanically most intimately. In consequence of its continuous work and productive power, the emulsor substitutes most satisfactorily stirring or other means of bringing about a mixture used in the tar industry, soap manufacture, &c. For the benefit of those who do not know the emulsor I will describe it before entering upon the experiments I have made with it.

The apparatus is very simply and substantially made, and easily managed when in use; it consists of two massive plates, turned towards each other, and fastened upon a vertical axle (see Fig.). The plates rotate with a rapidity of 6 to 7000 revolutions per minute. The opening between them may be increased or diminished from 0.05 m.m. to 1—2 m.m. By the size of this opening the grade of oil in the emulsion is regulated. If the opening be small, 0.05—0.01 m.m., a very fine emulsion is produced,—for instance, from olive oil and water. In this case the oil globules are much smaller than those in milk. From such an emulsion the fat is separated by gravity within 20 to 25 minutes, but if the water be alkaline the emulsion remains for a longer period. A larger opening produces a less fine emulsion, which separates itself in much shorter time, say in 2 to 3 minutes, if the opening be 1 m.m. The quantity produced is in proportion to the size of the opening, and varies from 300 to 2000 litres per hour. Previous to the making of an emulsion all mechanically introduced hard and coarse particles which cannot pass through the opening must of course be separated by filtering. Emulsions containing as much as 40 per cent of oil may be made, even up to 50 per cent of certain oils. On the other hand, one may mix five, ten, or even thirty per cent of water with the oil; consequently there is a limit for the emulsive process in reference to the quantitative proportions of the mixtures. Emulsions of water in oil become valuable when small quantities of salts or other agents in solutions of water are desired to act on the oil. The consumption of agents may in this way be reduced to the smallest possible quantity. Emulsions of water or salt solutions in oil made by the emulsor have several interesting qualities, of which I hope to speak further in a future article. The emulsor may be used either in an ordinary separator frame with a pulley (see Fig.), or else in a steam turbine frame, the latter being the most handy, as the machine will work simply by turning a steam valve.

The plates of which the emulsor consists are made from strongly tinned Swedish iron, or from iron with a preparation of antimony and lead, or from acid proof bronze: which material will be chosen depends upon the purpose for which the machine is intended. The plates may easily and inexpensively be replaced by new ones when worn out, which can only take place after a long and continuous use. Should they become rough from the action of acids, &c., they may simply be ground and tinned with antimony and lead, which will render them equal to new; and this operation may be repeated a great number of times on account of their extreme massiveness. Emulsor plates of Swedish iron are always used for acid emulsions in cases where small quantities of iron in the cleansing water do not harm the product. When used for alkaline emulsions and washings with water the plates will prove to possess great durability.

All other parts, frame, &c., are equally solid and con-

structed on the same principles as the "Alpha" milk separators.

The following is a brief account of experiments made by me for the purpose of ascertaining the fitness of the machine for the object intended, namely, intimate mixing of uncongenial liquids. The experiments are made with quantities varying between 50 and 300 kilograms.

SERIES A.—*Washing away of Free Mineral Acids from Oils and Fat.*

From Olive Oil.—To common machine oil I added 5 per cent of sulphuric acid of 1.50 specific gravity, and mixed this sour oil in water in such a way that an emulsion of about 20 per cent of oil was obtained. The opening between the emulsor plates was about 0.1 m.m. The emulsion separated itself in 10 to 15 minutes. After one more washing with fresh water the oil was free from acids, which was tested with litmus paper, after having shaken the oil with warm distilled water. The oil was at first not clear owing to the presence of air bubbles and drops of water, which all disappeared after the oil had stood for 24 hours undisturbed. One part of the oil was obtained free from water and air immediately, by filtering through newly burnt sulphate of lime.



CENTRIFUGAL EMULSOR IN SECTION.

The oil may be separated easily from the washing water with a receiver constructed on the principle of the Florentine flask, and capable of holding that quantity of emulsion, which is made in the time required for the oil to separate itself from the emulsion.

The washing-water contained in the above mentioned cases a small number of minute particles of oil; these could easily be collected in either of the following ways:—

1. By filtering through cotton-wool and boiling the wool in water, when the oil rises to the surface.
2. By leaving the washing-water undisturbed for about 48 hours, when all the oil will float on the top.
3. By mixing more olive oil with the washing-water and using a large opening. The large oil globules hereby produced brought the smaller ones with them to the surface and a clear washing-water remained. This way of separating minute particles of oil from the washing-water is very effective; even from alkaline washing-water could all oil be re-claimed by using mineral oil.

4. By centrifugal power in continuous oil separator with the same rapidity as the emulsor.

As I have shown, there was no difficulty in extracting the whole of the oil from the emulsion.

At a repeated experiment with olive oil, when 5 per cent of sulphuric acid of a specific gravity of 1.84 was used, all free sulphuric acid was washed away in two washings, one with warm and one with cold water. In this case, however, the oil was strongly affected by the acid.

From Tallow.—Raw tallow was melted and about 3 per cent of nitric acid was mixed into this. After two washings with water I got a pure, light, acid-free product. When the tallow had separated itself from the emulsion all cell fragments, &c., stayed underneath the pure tallow

as a well-defined layer. This way of separating membranes, loosened by the action of the acid, seems to come in very handily for refining tallow.

From Mineral Oils.—In a lubricating oil of a brownish colour I mixed 5 per cent of sulphuric acid of 1.84 specific gravity. The oil was then washed twice with water; the first washing-water had taken up much colouring matter. After a third washing with concentrated solution of caustic soda, I got an oil which had only a slight yellowish tint.

In another experiment I took raw vaseline from Galicia, melted it, and with help of the emulsor I mixed into it about 5 per cent concentrated sulphuric acid and some chromate of potassium, washed the vaseline with warm water, and then filtered it through a layer of bone-black 10 c.m. thick (to get rid of carbon particles and newly formed brown colouring-matter), and by this process I got an almost colourless vaseline.

SERIES B.—Washing away of Free Fatty Acids from Oils.

From Olive Oil.—I mixed the oil with water containing 0.5 per cent of caustic soda. The oil extracted from this emulsion was then washed in clean water and lastly in water with some sulphuric acid. After this process the oil was free from fatty acids.

Out of the first washing-water, which contained soap, a liquid fat consisting principally of fatty acids separated itself when acid was added.

From Hemp Oil.—This oil was treated in the same way, and was also made perfectly free from fatty acids.

SERIES C.—The Use of the Emulsor in Manufacturing Soap.

a. *Cocoonut oil* was mixed with a strong solution of caustic soda. This emulsion, already containing a great deal of fat in a saponified condition, yielded immediately on boiling a homogeneous soap.

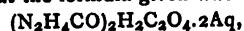
b. *Cocoonut oil* was warmed up to about 110° C. and then mixed with a solution of caustic soda at boiling-point. The result was a liquid containing a number of gas bubbles which caused an opalescence and hardened when cold. On examination it was found to contain no free fat, so that a perfect and almost immediate saponification had been obtained.

Results of later experiments with the emulsor in saponification of fat with sulphuric acid, washing of tar, &c., I intend to publish at an early date.

NOTE ON THE FORMULA OF UREA OXALATE.

By PATRICK H. KIRKALDY.

HAVING occasion to determine the carbon and hydrogen in urea oxalate, I found, on reference to "Bloxam's Chemistry," that the formula given was—



which gave the following percentages:—

Carbon .. 19.512 Hydrogen .. 5.691

The result of my first analysis of the oxalate, obtained by precipitation from a hot solution, was—

Carbon.. 22.16 p.c. Hydrogen.. 4.903 p.c.

which pointed to the supposition that the body was anhydrous, in which case the calculated percentages are—

Carbon .. 22.85 Hydrogen .. 4.76

A second analysis was then made of crystals obtained by allowing the mother-liquor to stand, when the results obtained were—

Carbon.. 23.04 p.c. Hydrogen.. 5.126 p.c.

A third analysis of some of the first crop of oxalate

crystals dissolved in as little water as possible and re-crystallised *in vacuo* gave the following results:—

Carbon.. 22.804 p.c. Hydrogen.. 4.787 p.c.

In order to further check the results I made two determinations of nitrogen in the re-crystallised oxalate. The calculated percentage in the anhydrous body is 26.67.

The results obtained from the re-crystallised product were—

(1) 27.38 } Mean, 26.94.
(2) 26.51 }

In conclusion, 1.3125 grms. of the air-dried re-crystallised oxalate were left *in vacuo* over H_2SO_4 for sixteen hours; no change in brilliancy took place, and only a slight loss in weight, amounting to 0.4 per cent.

0.659 of a gram. was left in a water-oven for two hours. The loss in weight resulting was only 5 m.grms., or 0.76 per cent, probably due to the partial decomposition of the body. It appears, therefore, from the results of analysis that urea oxalate is an anhydrous salt.

	Found.	Required for (N_2H_4CO) $_2$ $H_2C_2O_4$.
Carbon	22.804	22.85
Hydrogen	4.787	4.76
Nitrogen	26.94	26.67
Oxygen	—	45.72
		100.00

The following books make no mention of water of crystallisation:—"Watts' Organic Chemistry," "Miller's Elements of Chemistry," "Watts' Dictionary," "Dictionnaire de Chimie," by Wurtz, and "Cours de Chimie," by Gautier.

The following state that urea oxalate crystallised with 2Aq:—"Bloxam's Chemistry" and "Strecker's Organic Chemistry," while in "Booth and Morfit's Chemistry" the following formula is given:— $C_2H_4N_2O_2 + C_2O_3 + HO$, in which there seems to be some error.

Chemical Laboratory,
King's College, London, W.C.

THE CHANGE OF PRESERVED FERRUGINOUS MINERAL WATERS.

In a recent note (*Comptes Rendus*, cxiv., 1363), M. Parmentier very rightly emphasizes the well-known fact that mineral waters away from the spring undergo a change in the vessels which contain them, and he proposes a method for their better preservation. He says:—

I am not aware whether any experiments have been made which give an idea of the degree of change which takes place in transported mineral waters. It is, as we know, variable; but some years ago I had an opportunity of examining some ferruginous mineral waters from the point of view of their iron contents, and it is the result of these experiments made by a rapid method which I intend to state.

In order to be as much as possible in the ordinary conditions of therapeutic employment of these waters away from the spring, I took them in bottles from one of the best chemists of Paris. The vessel placed standing during the very short time requisite for the ferruginous deposit or that of other substances in suspension, is carefully opened, and 250 cubic centilitres of the limpid part is syphoned, where, immediately after acidification, the iron protoxide is estimated with a weak solution of permanganate, in accordance with the well-known prescriptions. In a second similar quantity tested, the total amount of iron is found after reduction by zinc and the same reagent.

This rapid procedure, so convenient and frequently employed for determining small quantities of iron, is not perhaps in this case quite free from reproach, on account

of the possible presence of organic or sulphurous substances in some mineral waters. But we know that in the cold the decolouration of permanganate by ferrous salts is instantaneous, whilst it is slow and progressive for most of the organic substances; this second phase of the operation serves even to verify its presence. Let us also observe that the action of organic substances tends to increase the amount of iron, but in this case the figures obtained would show *a fortiori*, as we shall see, that the iron dissolved has almost disappeared in most of the transported mineral waters.

The results of the experiments have been calculated in metallic iron, in solution, in a litre; this form is beyond all dispute and permits later hypothetical groupings. The results, besides, are placed opposite the metallic iron contained in a litre calculated according to the analyses of waters drawn from the spring, which are to be found in special publications.

Transported Mineral Water.

	Metallic Iron.		Water taken at
	Dissolved in state of protoxide. Grm.	Total after reduction by zinc. Grm.	Spring. Metallic Iron. Grm.
Auteuil	0'0007	0'0022	0'0809 (O. Henry père)
Busang	0'0000	0'0007	0'0082 (O. Henry)
Forges (Royale) ..	0'0000	0'0007	0'0041 (Willm)
" (Reinette) ..	0'0002	0'0010	0'0521 (Girardin)
Lamalon (Bourges)	0'0002	0'0059	0'0171 & Morin)
Orenna (Sorgenta Sotlana)	0'0000	0'0011	0'0050 (Bechamp)
" (2nd example)	0'0000	0'0004	0'0618 (Poggiale)
Pougues (St. Leger)	0'0004	0'0015	0'0618
Soultzbach (Alsace)	0'0000	0'0000	0'0072 (O. Henry)
Spa (Poutron). ..	0'0255	0'0260	0'0021 (Carnot)
Vals (Rigolette) ..	0'0002	0'0015	0'0112 (Oppermann)
(Dominique). }			
Vichy (Lardye) ..	0'0004	0'0011	0'0448 (Monheim)
			?
			0'0073 (Willm)

One can see from these few examples that most of the waters considered ferruginous lose, according to the present system of preservation, either all or most of their iron, which is precipitated, and the small amount which remains in solution is in the ferric state. It results that in many of the cases in question, and considered (to the exclusion of other principles) as a ferruginous re-constituent, the results may become unreliable from the therapeutic point of view, and some improvement in the method of preservation is necessary. Specialists have for a long time been studying this preservation, as shown by the numerous articles devoted to this subject in works on hydrology. It has been proposed to fill the vessels with a dipping tube, and expel the air by inert gases, chiefly carbonic acid (M. Porret). Some mineral waters are even surcharged with this gas. This last practice is not advisable, because it changes the nature of the water drawn from the spring.—*Comptes Rendus*, June 20, 1892.

Plumbiferous Glass-Wool.—L. Blum.—In the course of gas-analytic operations the author caused gases containing sulphuretted hydrogen to traverse a plug of fine white glass-wool, as obtained in commerce. The wool was blackened, and on further investigation it appeared that the blackening was due to the formation of lead sulphide. Hence a plumbiferous glass had been used for the production of the glass-wool. In various analytical operations where glass-wool is used the presence of lead is objectionable. Nor can such material be used, as recommended, for filtering acids, since they may become contaminated by taking up lead.—*Zeitschrift für Anal. Chem.*, xxxi.

THE EFFECT OF LIMING ON THE POROSITY OF CLAY SOILS.

By A. N. PEARSON,
Chemist for Lands, Agriculture, and Victorian Water Supply.

WHILE reporting recently on the site proposed for the establishment of a sewage farm in connection with the sewage scheme now being carried out by the Melbourne and Metropolitan Board of Works, I was led to consider how the porosity of the soil might be increased, the soil in many parts being a stiff clay. The amelioration of clay soils by means of liming is an old agricultural expedient, hence it occurred to me to ascertain definitely how much the porosity of clay soils was improvable by liming.

In testing the permeability of soils, certain precautions must be adopted, otherwise exceedingly discordant results will be obtained. The precautions I took were as follows:—The soils were all dried to the same degree of dryness, and were afterwards ground and sifted to the same degree of fineness. Care was taken that the soils in the different percolation tubes were compressed to the same degree of compactness; to this end the tubes, when being filled, were all inclined at the same angle, as shown at A in the diagram, so that in each case the soil ran down the side of the tube with the same velocity. The soil was filled up after two or three trials to $\frac{1}{4}$ inch above the mark, then the tube was slowly raised to an upright position, suspended between the finger and thumb of one hand, and gently tapped from below with the finger of the other hand, until the soil sank down exactly to the mark. It was found impossible to pour water down the tube even in a very fine stream without disturbing the surface of the soil. But any disturbance of the surface of clay causes a difference of porosity. To obviate this difficulty I covered the clay with a layer, $\frac{1}{4}$ -inch thick, of sand of uniform size. The water was run into the tubes by means of a water-bottle arranged as shown at B in the diagram, the delivery tube having attached to it a piece of indiarubber tubing acting as a syphon and furnished with a screw pinch and with a fine delivery jet. By this means the water could be delivered in the gentlest stream. With these precautions results were obtainable sufficiently accordant for my purpose.

The test adopted was to pour two inches depth of water on to two inches depth of dry soil, and to observe the time required for the water to disappear below the surface of the sand.

The differences in the time required with different soils were very great, as will be seen from the following examples:—(See Table I.).

To observe the effect of liming I mixed samples of the dried and sifted soils with $\frac{1}{2}$, $\frac{1}{4}$, and $2\frac{1}{4}$ per cents of quick-lime, then added water, worked into a paste, dried, ground up, and sifted, and tested for percolation as before. The results obtained are given in Table II.

It is certainly noteworthy that a soil such as No. 3, which in its natural state required from twenty-three to thirty-one days for two inches of water to percolate through it, allowed the water to pass through in an average of seven hours after the soil had been mixed with $2\frac{1}{4}$ per cent of lime. Perhaps, however, the most striking case is that of Sample No. 1, which in its natural state required six days four and a quarter hours for the water to pass through it, but when mixed with only a quarter per cent of lime required only twelve and three-quarter hours. Had the test consisted of pouring two inches of water on to wet soil instead of on to dry, the contrasts would have been still greater.

The application of lime to the soil of sewage farms situated in clay districts might be useful for more reasons than one; it would reduce the area required, render underground delivery possible where otherwise impossible, and probably assist materially in the purification of the sewage.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the

maina of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined, eleven were found to be very slightly turbid; the remainder being clear, bright, and well filtered.

It will be seen from the Tables that, owing doubtless to the occasional stormy rainfall of the month, several of the samples of water examined had to be described as "very slightly turbid," an expression made use of to signify such a deficiency in brightness as is recognisable only on careful examination. In other respects the entire number of samples examined were found to be of excellent quality, especially in regard to their maintained freedom from colour-tint and excess of organic matter. Thus, taking the Thames-derived samples for comparison, the mean proportion of organic carbon was found to be 0.107 part in 100,000 parts of the water, as against a mean of 0.119 part for the previous month; while the maximum amount of organic carbon in any single sample examined was found to be 0.134 part, as against a maximum for the previous month of 0.143 part, the insignificant differences in amount, or 0.012 part and 0.009 part respectively, being to that extent in favour of the June supply. The mean proportion of organic carbon present in the Thames-derived samples examined during the past half-year terminating on June 30th amounted to 0.131 part in 100,000 parts of the water, corresponding to less than a quarter of a grain of organic matter per gallon.

We are, Sir,

Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.

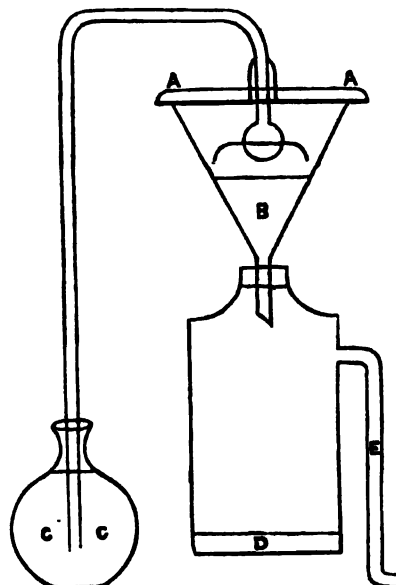
APPARATUS FOR WASHING PRECIPITATES. By MATTHEW FORBES.

THE following simple apparatus for the washing of precipitates will be found to be of much advantage, especially when washing gelatinous ones:—

Procure a lead disc about $\frac{1}{2}$ inch thick and a little larger than the funnel that is used, with a true face and a projection on the centre of the other side, with a hole bored through (*A*) to admit of a piece of glass tubing passing easily through; then blow a small bulb on one end of tube, and pierce four small holes with a needle through the side of it while held in the flame; then get a disc of the thinnest indiarubber and punch a hole smaller than the glass tubing, and pass tubing through both discs and projecting beyond the other side, and slip on a piece of indiarubber tubing to embrace both glass tubing and projection on lead disc; and to the other end of rubber tubing connect a convenient length of tubing to be led into a flask or jar of the washing fluid to be used. Now throw precipitate into funnel with ground face and wash it down on filter paper as much together as possible, and leave a little more fluid in funnel than you wish to have during washing. Now moisten the discs with water, and place on funnel, pressing firmly down and round a little, and start filter pump; the result of which will be that as the fluid is withdrawn from funnel the washing fluid in flask will pass over to replace it (if all the joints are air-tight),

and will now wash as long as you choose simply by keeping flask supplied with washing fluid, and leaving one free to work at something else.

The apparatus washes very quietly and does not disturb the precipitate, the fluid acting more as a series of layers of fluids passing through precipitate.



- A, Lead and rubber discs
- B, Precipitate and fluid.
- C, Washing-fluid.
- D, Filtrate.
- E, Tube leading to filter pump.

In the event of the small bulb dipping into the fluid in funnel, lift out tubing from the flask before stopping filter-pump, as otherwise some of the precipitate might be carried back to flask when filter-pump is stopped.

The accompanying sketch will give a clear idea of the apparatus.

ON NATURAL PHOSPHATES.*

By J. LAINSON WILLS, F.C.S.

(Concluded from p. 47).

Nodular, Concretionary, and Arsenaceous Phosphates.

THESE are by far the most important of nature's phosphatic reserves, comprising as they do the South Carolina deposits, the French deposits of the Somme, Ardennes, and Meuse, the Belgian fields of Mons and those more lately opened up at Liege (Hesbaye). The so-called "Bordeaux phosphates," because being formerly shipped from that port, but having their real origin in the region of Quercy, comprising portions of the departments of the Lot, Tarn, and Garonne, and Aveyron, also furnish a considerable quantity of nodular or phosphatic concretions of kidney shape, of great purity (88 per cent), and curious geological interest. These are well represented by specimens on the table, and coming from the crevices in the Oolitic limestones, accompanied by *débris* of Tertiary age (Eocene), the walls of the crevices or fissures being at the same time incrustated with phosphorite of a high degree of purity, attaining 80 per cent of tribasic phosphate of lime.

We must not omit here the Florida nodular beds of land and river formation, which are now enjoying such a glorious boom.

As a peculiarity of this Bordeaux phosphorite, we may mention that it contains a very appreciable proportion of iodine.

The Russian deposits, situated between the rivers Desna and Don, occur in the Cretaceous system, at about the same horizon as the Cambridgeshire coprolites, and may be described as nodular.

The Nassau or Lahn concretions in clay are of Tertiary age, and although not exhibiting signs of organic remains, are generally believed to be of animal origin; they attain 60 to 75 per cent phosphate of lime, but are too ferruginous to be much in request for superphosphate manufacture.

The Belgian (Ciply) deposits, which have furnished over 150,000 tons per annum of a 40 to 50 per cent product, are of a nodular character, although the grains are often so fine as to be considered more correctly arenaceous.

The same may be said of the very remarkable French deposits, discovered near Amiens in 1886, and known as the Somme phosphates. These are granular or arenaceous, and to this feature, as well as to their richness (65 to 80 per cent), may be attributed the enormous development which they have enjoyed in such a short period, attaining the annual production of 200,000 tons.

Conglomerates and Breccias.

Phosphatic beds may also assume these characters: sometimes with the cementing material as the phosphatic element, and at others with the enclosed pebbles or angular fragments as the valuable portion for commercial supplies.

Thus the Cambridgeshire coprolite fields furnish a conglomerate of phosphatic pebbles, cemented by ferruginous sand, while in the Ardennes district (France), is found a peculiar agglomeration of granules of chlorite in a phosphatic cement, the whole yielding 40 to 45 per cent phosphate of lime.

The Belgian (Ciply) deposits yield abundant supplies of a mass of phosphatic nodules, shells, casts, and fossils, cemented in a calcareous matrix, to utilise which has puzzled the ingenuity of many an "exploitant."

Phosphatic Limestone and Marls

Are found in most strata from the Silurian epoch down to more recent time.

The metamorphosis or transmutation of earthy carbonates into phosphates is a very simple and comparatively rapid process, and the evidence of Dr. R. Ledoux in the following description is instructive. He says in a recent article on phosphates: "Some clients of mine sent a ship to a coral island in the Southern Pacific to bring away a cargo of bird guano. The birds were still in countless thousands. The captain had been there for a load twenty years before, and since that time no guano had been removed. At his first visit the crew had cleaned off a space and made a house of coral rock, covering it with a sail, and had used it for a shelter and storehouse while at work. On leaving, the sail was taken away and the walls and board floor left. On the return, twenty years after, there was an average depth of twenty inches over the floor—an inch a year. The underlying limestone was altered into phosphate for a depth of several feet, but the conversion of carbonate into phosphate gradually became less perfect as depth from surface was attained."

I have observed the same effect myself taking place in the West Indies, where the surface of the coral rock is speedily converted into phosphate of lime, wherever the sea-birds are in the habit of congregating.

Such indeed is the simple origin of some of the most important deposits of phosphate in that portion of the world, i.e., Curacao, Sombbrero, and Aruba, &c.

The prospecting and first development of the latter named island having fallen to my own care and experience, I am able to produce some interesting specimens here, illustrating very clearly the history of their formation, by examination of their fossil organisms, originally carbonate

of lime (coral rock), and now seen to be, by analysis, phosphate of lime of over 80 per cent.

The deposits of Florida and South Carolina would appear to owe much of their phosphatic wealth to *débris* of phosphatised limestones and marls.

One of nature's operations, which is a factor in enriching already formed phosphate beds, may be here alluded to, namely, the property of spring waters (which often contain considerable proportions of bicarbonates and free carbonic acid) to dissolve neutral carbonate of lime, even when presented to them in apparently as the most compact and impervious material. Such has been the origin of the many remarkable caves existing in the limestone rock formations (Cheddar, Derby, Kentucky, &c.).

This property applied to a calcareous phosphated material will, in course of time, ablate, as it were, more carbonate than phosphate, and to this action is attributed the value of many thousand tons of material, in such extensive beds as those of the Somme, Ciply, Liège, and probably of Florida.

While speaking of these beds of the Cretaceous period, I may mention the recent opening up of another similar field in France. I refer to that in the department of the Pas de Calais, which would appear to be of the same nature as that of the Somme.

Apatites.

Although crystallised phosphate of lime is found as a component of rock masses in more recent strata, yet we do not yet know of any workable deposits of this mineral before passing to the oldest of fossiliferous systems, the Laurentian.

The rocks of this formation are among the most ancient on the North American continent and probably correspond to the oldest gneiss of Scandinavia. The modes of occurrence are so varied in the Canadian apatite field, that the subject would require to be treated by itself in order to do it justice here.

We are all here familiar with how it is found, both in Ontario and Quebec provinces.

Dr. Hunt thus describes, in 1884, the main features of its mode of occurrence;—"The deposits of apatite are in part bedded or interstratified in the pyroxenic rock of the region, and in part are true veins of posterior origin. The gneissic rock with their interstratified quartzose and pyroxenic layers, and an included band of crystalline limestone, have a general north-east and south-west strike, and are much folded, exhibiting pretty symmetrical anticlinals, and synclinals, in which the strata are seen to dip at various angles, sometimes as low as 25 degrees or 30 degrees, but more often approaching the vertical. The bedded deposits of apatite, which are found running and dipping with these, I am disposed to look upon as true beds, deposited at the same time with the enclosing rocks. The veins, on the contrary, cut across all these strata, and in some noticeable instances include broken angular masses of the enclosing rocks. They are, for the most part, nearly at right angles to the strike of the strata, and generally vertical, though to both of these conditions there are exceptions. One vein, which had yielded many hundred tons of apatite, I found to intersect, in a nearly horizontal attitude, vertical strata of gneiss, and in rare cases what appear from their structure and composition to be veins are found coinciding in dip and in strike with the enclosing strata."

The apatites of Norway are known since 1854, and occur on the southern coast in similar rocks to our own (Canadian), and many of the associated minerals are similar to those observed in the Laurentian rocks, the vein matter differing chiefly in freedom from carbonate of lime.

Rutile may be mentioned as an exception, which in some minds is so abundant as to form a considerable revenue to a working mine, since it is worth 1s. 6d. per lb., say \$800 per ton. These are fluor-apatites, although they contain also some chlorine.

Continental geologists (Brogger and Rensch) who have studied these formations have supposed them to be of eruptive origin, in consequence of the absence of phosphoric acid in the surrounding rocks, but the question seems to be most doubtful, as well here as in the case of the same opinion held on the Canadian apatite deposits.

The Situation of Canadian Phosphate Trade.

Although this Canadian industry has not progressed on the same scale as many other phosphate fields, Somme, Ciply, Liège, Carolina, and Florida, yet there are some facts offering an explanation for this. The peculiarity of the occurrence of the mineral in vein-like formation in hard rock, calls for a scientific and economic system of mining, which has been little applied to the development of our deposits, and the cost of production is thereby more considerable than that attained in other fields of supply.

Certain centres of manure manufacture still require our high testing products to complete their standard types of concentrated supers, and the rapidly increasing demand for fertilisers by all the civilised world, both the new and the old, will tend to maintain a fair value for natural phosphates. We are getting into the era in which steam does not work fast enough, and on every hand we are seeking to accomplish our ends by electricity with lightning speed. Someone has said that the man who could make two blades of grass grow where one grew before was a benefactor to his race, but the rush and the struggle for existence imposes that every cultivator shall be a benefactor in this regard, and carry on agricultural science at the highest possible tension for his very existence.

With increasing populations, with better means of transport, and lastly, but not least, advanced scientific education, fertilisers and all other artificial means of stimulating our exhausted soils will continue to be in increasing demand.

We see no reason, therefore, to suppose that the mineral phosphate industry or phosphate mining has attained its zenith, and so far as we can see at present, the future demands of the world for phosphoric acid are destined to increase with time and agricultural progress.

Résumé.

We may shortly generalise the foregoing facts and observations.

Of the sixty-four elementary substances at present known to compose the material of our original globe, phosphorus is found to be among the twenty more abundant elements, and is recognised to have been widely disseminated in all the original and ancient rock masses. With the exception of the segregations of crystallised apatite in the Laurentian rocks, we do not find any marked local accumulation of phosphatic bases in any of the azoic formations or intrusive rocks.

The existence of the Bozoon Canadense is still debatable, and it is problematical whether the apatite of these older metamorphosed strata is not the mineralised product of organic remains, but passing from the Laurentian epoch to the succeeding and less altered rocks we are immediately in presence of abundant evidence of organised life, and cannot fail to remark how much more frequent are the accumulations of phosphatic beds.

The function of organised life to assimilate and concentrate the disseminated phosphoric element is strikingly apparent. The natural forces which are ever restless and continual in building up the varied geological strata of succeeding epochs (attrition, deposition, cementation, ablation, &c.) may alter and vary the manner of presentation of the phosphatic deposits which we have been considering, but the silently working power of assimilation by the organised cell would appear to triumph over the mighty disruptive and more violent operations of nature, for the latter forces fail to re-disseminate the work accomplished by the former, but rather complete the task required to secure to man the providential supplies of phosphatic deposits with which we may satisfy our pre-

sent demands, and therefore these economic supplies are seen to be chiefly in the more recent geological formations.

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 48).

MANY varieties of cupric oxide were examined. Material obtained from the carbonate, or by precipitation from the sulphate, evolved little or no gas, thus affording an admirable proof of the purity of the acid and water. Check experiments with such material were accordingly made from time to time. Other circumstances being equal, the purer the oxide the more gas was evolved. Solid impurities, such as alkaline salts, seemed partially to prevent the occlusion.

The volumes of gas are given without any correction, the temperature and pressure remaining so nearly constant that the observations are not recorded. The following Table is intended only as a basis of rough comparison. The gas was frequently analysed, with results similar to those tabulated above. The results confirm those of the preceding series.

The higher temperatures recorded above are merely approximate guesses. 600° signifies a dull red heat, 700° a medium red heat, and 900° a very bright red heat. In Experiment 92 the oxide was heated at the highest temperature obtainable by a Berzelius spirit lamp. In No. 94 the material was heated for an hour and a half in the Berzelius lamp, and then for an hour in a glass tube under a stream of oxygen. The oxide was transferred while warm to the bulb apparatus. It evolved upon solution 0.088 per cent of gas, one-eighth of which was oxygen. In the ninetieth experiment hydrochloric acid was used for the solution of the oxide.

The two series of determinations, which were perhaps more numerous than necessary, showed the following important facts:—

First, that cupric oxide prepared by the ignition of the oxy-nitrate after Hampe's method contained between four and five times its volume of occluded gas. (Nos. 58, 63 to 67, 84 to 94).

Second, that ignition of the oxide at very bright redness was capable of expelling a portion of this gas. The temperature required was nevertheless considerably above that which Hampe apparently employed. Nos. 59, 81, and 95).

Third, that beyond a certain limit the time of ignition makes no important difference. (Nos. 86 to 91).

Fourth, that the gas was not absorbed from the air on cooling. (Nos. 64, 65, 66, and others).

Fifth, that specimens of cupric oxide prepared in different ways contained very different amounts of gas. It is a curious fact that material which has been heated only to 300° contained less gaseous nitrogen than that which had been ignited at a higher temperature. In this case the nitrogen may still have existed in the combined form. (Nos. 78, 79, 84, 85).

An explanation for the observed phenomena must necessarily be hypothetical, and will not be attempted at present.

In order to find the direct connection between the loss of weight noticed upon heating cupric oxide and the quantity of gas retained by the substance, the following experiment was made:—

Experiment 101.—Cupric oxide which had been heated to constant weight at dull redness was ignited at bright redness in a double platinum crucible.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

Occluded Gas in Cupric Oxide.—Second Series.

No. of experiment.	Nature of cupric oxide.	Weight of CuO. Grms.	Heat and time of ignition.	Volume of gas evolved. C.c.	Per cent of gas in CuO by weight.	Remarks on method.
68	Blank experiment.	—	—	0'00	—	H ₂ SO ₄ + H ₂ O.
69	" "	—	—	0'00	—	"
70	Precipitated.	1'00	Dull red.	0'10	0'011	Bulbs.
71	" "	1'60	"	0'20	0'013	"
72	From carbonate.	1'50	Dull red.	0'07	0'006	Bulbs.
73	" "	2'00	Dull red exposed to air.	0'10	0'006	"
74	{ Crude, of commerce, contained cuprous oxide. }	3'00	Not ignited.	0'70	0'026	Bulbs.
75		8'00	Dull red.	2'00	0'028	Flask.
76		7'00	Not ignited.	2'00	0'032	Another sample.
77	From carbonate.	1'50	Dull red.	0'05	0'003	Flask.
78	{ Six experiments with CuO prepared by action of CuO on Cu(NO ₃) ₂ and sub- sequent ignition of basic nitrate. }	1'70	Very low.	0'34	0'023	Flask.
79		3'20	Dull red, 3 hours.	1'03	0'036	"
80		1'20	Dull red, 7 hours.	0'25 (?)	0'023 (?)	"
81		1'70	Bright red.	0'09	0'006	"
82		2'00	Dull red.	0'26	0'015	Pump not used.
83		2'00	"	0'73	0'042	" "
84	After Hampe's method.	0'39	310°; 2 hours.	0'27	0'050	Bulbs.
85	" "	1'28	" "	0'30	0'035	"
86	" "	1'88	600°; 2 hours.	1'35	0'084	Flask.
87	" "	0'39	700°; ½ hour.	0'30	0'087	Bulbs.
88	" "	0'50	600°; 1 hour.	0'33	0'077	"
89	" "	0'60	600°; 4 hours.	0'41	0'079	"
90	" "	0'61	" "	0'36	0'070	Used HCl.
91	" "	0'44	" "	0'29	0'079	Bulbs.
92	New preparation.	2'00	700°; ½ hour.	1'37	0'080	See above.
93	" "	2'98	600°; 2 hours.	2'12	0'082	Flask.
94	" "	0'98	See above.	0'75	0'088	See above.
95	" "	0'50	900°; 1 hour.	0'17	0'039	—
96	{ From carbonate pre- pared from nitrate. }	0'65	600°; 1 hour.	0'09	0'016	—
97		0'50	290°.	0'10	0'023	—
98	{ From carbonate of com- merce. }	1'00	600°; 1 hour.	0'10	0'011	—
99		0'75	" "	0'03	0'004	—
100	Wire form.	1'00	—	0'01±	0'001±	Contained Cu ₂ O.

	Grms.
Weight of platinum crucible	= 18'0889
Weight of crucible + CuO, 2½ hours at dull redness	= 19'65852
Weight of crucible + CuO, 4 hours more at dull redness	= 19'65846
After ignition at very bright redness (30 minutes)	= 19'6574
After ignition at very bright redness (50 minutes more)	= 19'6571
Total loss of weight	= 0'0014

One gram. of this specimen was shown to contain 0'00081 gram. of occluded gas before ignition and 0'00039 gram. afterward (Experiments 86 to 95). In the quantity taken above, this difference corresponds to a loss of weight of nearly 0'0007 gram., or about half of that observed. The remainder of the loss may have been due to a partial reduction of the oxide. (Compare page 27).

Experiment 102.—In order to discover if heating cupric oxide in a vacuum produced any important evolution of nitrogen, six grms. of cupric oxide were dried in a glass tube with the greatest care, exactly after the manner of Hampe, and weighed in the air. One end of the tube was then sealed, the other was attached to a Sprengel

pump, and the whole was heated to about 500° C. for half an hour. Upon sealing and weighing, the loss of weight was found to amount to 4'4 m.grms. The amount of air displaced was found by opening the tube under boiled water, which wholly filled it. The weight of water, reduced to 4°, was 3'48 grms., while the temperature and pressure of the air at the time of weighing the exhausted tube were respectively 24° C. and 754 m.m. Hence the weight of displaced air must have equalled 4'1 m.grms., or only 0'0003 gram. less than the loss of weight actually observed. Therefore the cupric oxide could not have lost more than 0'005 per cent of its weight under the treatment described. The moist cupric oxide yielded approximately the usual volume of nitrogen upon solution in acids; but no very accurate measurement was made.

(To be continued).

Reproduction of Purely Potassic Nepheline.—André Duboin.—On continuing his researches on the reactions of silica or potassium hydrofluosilicate upon alumina in presence of an excess of melted potassium fluoride, he has succeeded by prolonging the action of the temperature in obtaining purely potassic nepheline, KO, Al₂O₃, 2SiO₂.—*Comptes Rendus*, cxv., No. 1.

* In Experiment 50 the temperature of ignition was somewhat higher.

METHODS OF SUGAR ANALYSIS.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION
OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

(Continued from p. 45).

ELECTIVE METHODS.

PLAN A.—Directions for the Examination of Syrups which
Contain 2 per cent or more of Invert Sugar, Starch
Sugar, or Raffinose, as also of Sugars containing
Raffinose.*

IN the examination of those syrups, which have been handed over to the chemist because they contain a per cent or more of invert sugar, the determination of the specific gravity and degree Brix can be made as previously directed. Naturally the direct determination of the specific gravity by means of the picnometer can take the place of this method, but in no case is it allowable to substitute the estimation of total solids, as on the one hand this would cause differences in the coefficient of purity as obtained by the officers and chemists, and on the other hand the determination of total solids in syrups containing invert sugar is much too difficult and takes up too much time to be of any use in every day practice. In calculating the coefficient of purity the method used in the sugar-house, namely, considering only sucrose as sugar, cannot be used, but the invert sugar must be calculated as sucrose by deducting one-twentieth of the amount found, adding to the direct content of sucrose and basing the calculation of this result.

For the determination of the sugar-content various methods can be applied according to the amount of invert sugar, starch sugar, or raffinose present. The following remarks will offer some explanation:—

The invert sugar of syrups is very often inactive, but can nevertheless have the power of rotating to the left, which deviation, according to late investigations, is 0.33, according to others 0.34 times as great as the right-handed rotation of sucrose. Consequently, as soon as considerable invert sugar is present, the polarisation of the sucrose present will be correspondingly diminished. As is well known Meissl proposed in the examination of colonial sugars to multiply the invert sugar found by 0.34, add this to the polarisation, and thus arrive at the correct amount of sucrose. This method would, however, be out of place in the analysis of syrups, as the invert sugar present very often does not show its normal rotatory power, but varies down to complete inactivity. Meissl's correction in such cases would lead to unreliable results. At the same time the rotatory power of the invert sugar may cause the results to be too low. In considering all these circumstances it becomes obvious that the determination of total sugar from the polarisation, and the invert sugar found, is only possible when the invert sugar present does not exceed a certain percentage. For instance, if 6 per cent of invert sugar were present the amount of sucrose could be $6 \times 0.33 = 1.98$ per cent too low. Therefore, as the syrups handed to the chemist for examination may contain considerable quantities of invert sugar whose rotatory power we do not know, we recommend the rejection of the optical method completely, and the adoption of a gravimetric one, a new and easy modification of which will be given under I.

The presence of starch sugar or raffinose makes a difference. The reducing power of starch sugar, which in the commercial article presents a variation corresponding to from 40—60 per cent of sugar, is not changed by the conditions under which the inversion of sugar syrups is made in the gravimetric method; and as we cannot determine the quantity of starch sugar present accurately, the gravimetric method for the estimation of the total content of beet sugar and of the quotient of purity is no longer applicable. It would, on the contrary, lead to

large errors, and syrups having a coefficient of purity of over 70 would, if examined by this method, after the addition of a certain quantity of starch sugar, appear to be below 70. In such cases, where starch sugar is present, the influence exerted by the lævo-rotation of the invert sugar upon the polarisation can no more be considered, as starch sugar has a higher dextro-rotatory power than the other sugars present. To avoid mistakes, which could be easily caused by adding starch sugar to syrups of a coefficient of purity of over 70, it is best, when starch sugar is present, to calculate the real sucrose content from the polarisation and the invert sugar directly determined. This method is described under II. If raffinose is present still another method, which will be found under III. must be adopted.

I.—The Presence of Starch Sugar need not be considered.

The examination of syrups which do not contain any starch sugar syrup will be a common occurrence, as such an addition is generally not made by the manufacturers themselves, but rather by the dealers. One operation will here suffice for the determination of total sugar.

Weigh out one-half the normal weight (13.024 grms.) of syrup, dissolve in a 100 c.c. flask in 75 c.c. of water, add 5 c.c. hydrochloric acid (38.8 per cent HCl), and warm in a water-bath to 67—70° C. As soon as the contents of the flask have reached this temperature heat for five minutes, not allowing the temperature to rise above 70° C., and shaking frequently. As the previous warming will take from two and a half to five minutes, the whole operation will require from seven and a half to ten minutes. Fill up to the mark, shake, and dilute 50 c.c. of this solution to a litre. By means of a pipette, transfer 25 c.c. of this to a flask and add 25 c.c. of a solution of sodium carbonate (1.70 grms. anhydrous salt to the litre) to neutralise

Table for Calculating the Sucrose corresponding to the
Invert Sugar Present from the Copper Found on
Three Minutes' Boiling.

Sucrose. M.grm.	Copper. M.grm.	Sucrose. M.grm.	Copper. M.grm.	Sucrose. M.grm.	Copper. M.grm.	Sucrose. M.grm.	Copper. M.grm.
40	79.0	73	145.2	105	208.6	139	269.1
41	81.0	74	147.1	107	210.5	140	270.9
42	83.0	75	149.1	108	212.3	141	272.7
43	85.2	76	151.0	109	214.2	142	274.5
44	87.2	77	153.0	110	216.1	143	276.3
45	89.2	78	155.0	111	217.9	144	278.1
46	91.2	79	156.9	112	219.8	145	279.9
47	93.3	80	158.9	113	221.6	146	281.6
48	95.3	81	160.8	114	223.5	147	283.4
49	97.3	82	162.8	115	225.3	148	285.2
50	99.3	83	164.7	116	227.2	149	286.9
51	101.3	84	166.6	117	229.0	150	288.8
52	103.3	85	168.6	118	230.9	151	290.5
53	105.3	86	170.5	119	232.8	152	292.3
54	107.3	87	172.4	120	234.6	153	294.0
55	109.4	88	174.3	121	236.4	154	295.7
56	111.4	89	176.3	122	238.3	155	297.5
57	113.4	90	178.2	123	240.2	156	299.2
58	115.4	91	180.1	124	242.0	157	300.9
59	117.4	92	182.0	125	243.9	158	302.6
60	119.5	93	183.9	126	245.7	159	304.4
61	121.5	94	185.8	127	247.5	160	306.1
62	123.5	95	187.8	128	249.3	161	307.8
63	125.4	96	189.7	129	251.2	162	309.5
64	127.4	97	191.6	130	253.0	163	311.3
65	129.4	98	193.5	131	254.7	164	313.0
66	131.4	99	195.4	132	256.5	165	314.7
67	133.4	100	197.3	133	258.3	166	316.4
68	135.3	101	199.2	134	260.1	167	318.1
69	137.3	102	201.1	135	261.9	168	319.9
70	139.3	103	202.9	136	263.7	169	321.6
71	141.3	104	204.8	137	265.5	170	323.3
72	143.2	105	206.7	138	267.3		

* Official German method used in taxing sugars (Zcit. Anal. Chem., vol. xxviii., No. 2.

the free acid present. Add 50 c.c. of Soxhlet's solution, heat to boiling, as in the determination of invert sugar, and keep the liquid in ebullition for three minutes. As all the sucrose in this solution has been inverted, and is therefore unable to influence the result, we need not be so careful about the time of boiling. Soxhlet's experiments show that two or three minutes difference will not influence the result materially. Dilute the liquid with an equal volume of water, which has been previously boiled so as to expel air, and continue as directed under the determination of invert sugar. The tables so far published for the calculation of results are of no value in this case, as they have been constructed with regard to glucose or a mixture of invert sugar and saccharose. The following table has been compiled for invert sugar, and enables the analyst to calculate the amount of sucrose directly from the amount of copper found.

Example: 25 c.c. of the solution = 0.1628 grm. substance, gave 0.1628 grm. of copper, which corresponds to 0.082 grm. of sugar. Therefore the syrup contained 50.4 per cent sugar.

Supposing that this syrup showed 80° Brix, then its coefficient would be 63. This coefficient is only calculated to tenths, hundredths in the case of the degree Brix being taken as an additional tenth, while with the co-efficient they are not considered, thus 82.85 Brix would be read 82.9, while a coefficient of 69.99 is taken as 69.9, and not 70.

(To be continued.)

THE PROPOSED "HOFMANN HOUSE."

THE German Chemical Society, in seeking to do well-merited honour to their late illustrious president, Prof. August Wilhelm von Hofmann, have struck out a new idea. They are not content with erecting a monument, column, obelisk, or the like at his grave or in some conspicuous place in Berlin. Their project includes, indeed, a splendid statue of the defunct discoverer, but it comprises something much more practical,—something to which the sternest utilitarianism of the old school could not object!

The Hofmann House is to include, in the first place, a locality—and we may presume a fully-equipped locality—for chemical investigations. Numerous and well arranged as are the laboratories of modern Germany, the Berlin Chemical Society conceive that erecting another not specially attached to any of the Universities, and connected with the reminiscences of Hofmann, will be a graceful tribute to the memory of him we have lost and a useful way of continuing his labours.

Another object of the proposed "Hofmann House" is to afford an occasional home for other scientific associations. Hence we presume that lectures, scientific congresses, demonstrations, and exhibitions will find here a welcome.

We need scarcely add that no nobler way of doing posthumous homage to a man like Hofmann could be devised.

We have had in this country men whom we might well have honoured in a similar manner.

The Institute of Chemistry of Great Britain and Ireland.—At the examination in Practical Chemistry for admission to the Institute, held from Monday, 11th, to Friday, 15th July, thirty-seven candidates presented themselves, of whom the following nineteen were successful:—Mr. E. C. Baly, Mr. F. J. Bloomer, Mr. A. C. Chapman, Mr. J. C. Chorley, Mr. F. Dent, Mr. F. E. Francis, Mr. A. F. Fryer, Mr. F. J. Hamby, Mr. E. E. Johnson, Mr. T. Kendrew, Mr. C. Leigh, Miss E. J. Lloyd, Mr. H. H. Mann, Mr. C. H. New, Mr. T. H. Norris, Mr. W. Orr, Mr. N. S. Rudolf, Mr. W. D. Sowers, and Mr. A. E. Wareing.

PROCEEDINGS OF SOCIETIES.

THE SOCIETY OF CHEMICAL INDUSTRY.

THIS Society has just held its Annual General Meeting on the 20th, 21st, and 22nd instant, under the Presidency of Dr. J. EMERSON REYNOLDS, F.R.S. The meeting was very numerous attended; indeed, it is probable that this will always be the case with London meetings. A member, *e.g.*, living in Manchester, if the meeting is not held in his own city, would much rather go to London than to Bristol, Newcastle, or Glasgow.

The meeting of the Council took place on Wednesday, July 20, at 2.30 p.m., in the Hall of the Drapers' Company, Throgmorton St., City, and the General Meeting at 3 p.m.

A reception by the President ensued at 8 p.m. in the galleries of the Royal Institute of Painters in Water-Colours, Piccadilly, W., followed at 8.30 p.m. by a smoking concert.

The second day was devoted to visits to works on the Thames. Two only of the works visited, those of the Union Oil Mills and of the Lindé Ice Works, could, strictly speaking, be called chemical works.

The excursion to Windsor and Cliveden was held on Friday, July 22nd, amidst brilliant weather, and was splendidly successful. The number of members and friends present was estimated at 500. The only drawback on this occasion was a lack of punctuality, due, we must add, not to the Council, to the efficient general secretary, Mr. C. G. Cresswell, or the London honorary secretary, Mr. J. Heron, but to the dilatoriness of some of the members and their friends. The special train for Windsor was timed to leave Paddington Station at 9.50 a.m., reaching the Royal Borough about 10 a.m. In sober sadness the train started only about 10 a.m., those who had already taken their seats having had their ears regulated with the hammering, consequent upon repairs, of the iron roof of the station.

At Windsor the scenery was unusually beautiful owing to the glowing sunshine following upon the rains in the earlier part of the week. The State Apartments, the Terraces, and the Round Tower were duly visited. At 12 noon an organ recital took place in St. George's Chapel. At 1 o'clock ensued luncheon in the Town Hall, the use of which was kindly granted to the Society by the Worshipful the Mayor of Windsor, J. Brown, Esq.

At 2.40 p.m. the party went down to the Quay and embarked in steam launches for Cliveden, the seat of the Duke of Westminster. The hill sides, covered with a rich and varied growth of trees and shrubs, were universally admired. Tea was partaken of in the "Cottage" in the woods, by the kind permission of the Duke of Westminster.

The return voyage was not quite felicitous. On approaching Boulter's Lock it was found that four launches were just in front, whilst a fleet of barges were coming in the opposite direction. "First come first served" is the sensible rule of the Conservators, so the party had to submit to heavy demands upon their patience.

NOTICES OF BOOKS.

Transactions of the Canadian Institute. No. 4. April, 1892. Vol. II., Part 2.

A GREAT part of the subject-matter of these *Transactions* lies quite outside the boundaries of Science.

Two papers on the "Yellows in Peaches" and on the "Blood of the Amphibia" are, of course, biological. The paper on the "Possibilities of Iron and Steel Production in Ontario" is not so much technical as commercial or economical. The "Contributions to Geology" consist of references to papers in the *Transactions* of the Canadian Institute.

CORRESPONDENCE.

AN OBSTACLE TO SCIENTIFIC PROGRESS.

To the Editor of the Chemical News.

SIR,—Dr. Gore's suggestive remarks upon this subject are framed in the spirit of appreciative criticism, and I venture to follow him with a few reflections which I believe to be similarly animated.

A short time since I happened to take the silent part in a conversation between a well-known M.P. and a distinguished member of the late (as of the next to be) government. The subject was the "latest mistake" of the present government, and upon this the ex-minister delivered himself as follows:—"Having been a member of more than one Cabinet I am always prepared to find sixteen men in conclave deciding upon that which each individual would consider an act of folly."

In this reflection it was not the party man but the philosopher who spoke, and the truism is as general to the scientific as to the political world.

No chemist in this country would call in question for a moment the capabilities or the motives—in respect of the discharge of official duties—of the individuals composing the Councils or Committees who administer the affairs of our learned or professional societies, nor hesitate to concede, *a priori*, that their collective judgment on any matter of the science was considerably more trustworthy than his own. But history, on the other hand, written or unwritten, would not confirm him in an uninquiring trust in the collective wisdom of these bodies *in action*. They are frequently worsted in controversy with individuals in smaller matters, and on broad questions of policy evince an indecision and want of grasp which compel the individual to reason, as the ex-minister above quoted, that a council of able men may be "an ass"—to use with due reservation and apology the classic simile.

Dr. Gore preaches forcibly the essential individualism of scientific work and progress; our learned societies, on the other hand, legislate for average truth and the average man, the non-existent individual born of statistics and convention.

Dr. Gore upholds, between the lines, that where there is no prophet the people perish. The Institute of Chemistry inculcates the lively doctrine that where there are no profits the chemist perishes. We must look to the Chemical Society to look after the prophets and the S.C. must consistently apply trades union principles for the purpose of raising profits. There is not doubt the Chemical Society can do much more than it does towards the encouragement of research; but, more important still, the individual chemist can do much to encourage the Society to encourage original enterprise, by quietly contributing to the breaking down of the "fixed ideas" by which it is generally, and the "conspiracy of silence" by which it is occasionally, dominated. The crusade undertaken by the Institute is of course based upon utilitarianism and expediency, and may be left out of consideration as a progressive movement of the Science *qua* Science. For such progress the world has to look to the individual worker; the individual wants liberty and opportunity, and too often meets with restraints and "mild repression." Dr. Gore has called attention to the existence of such obstacles to progress; he has stated his case temperately, and his statement will be the more likely, therefore, to command attention at head quarters.—I am, &c.,

X.

AN OBSTACLE TO SCIENTIFIC PROGRESS.

To the Editor of the Chemical News.

SIR,—No more important matter of general interest has, I fancy, appeared in your pages for some time than the

article by Dr. Gore, F.R.S., in the *CHEMICAL NEWS*, vol. lxi., p. 39. Much the same ideas suggested themselves to me on reading Lord Rayleigh's account of Mr. Waterston's paper in *Nature* a few weeks ago. The tendency to fixedness of habitual thought no doubt becomes greater and greater as the individual brain loses its plasticity; and this law perhaps explains why we have so constantly to deprecate the reluctance of seniors in a science to recognise the work of a junior, if it happens not to be "orthodox." I have had occasion, and shall have soon occasion again, to say strong things upon this subject; for the evil is magnified where "the interested influence of a close profession" comes into the court of judgment. The moral of the whole thing is (1) that we want a research department of a purely *professorial* character, such as we hope to see in the University of London in the future; (2) that the "*referee system*" which prevails in some of the "learned societies" has broken down, and needs to be superseded by standing "committees of publication," such as are in vogue at the Chemical Society. The responsibility is too much for an individual referee, especially if he is the nominee of the President, and it becomes a matter of course for the council to simply endorse and act upon his judgment.—I am, &c.,

A. IRVING.

Wellington College, July 25, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 1, July 4, 1892.

Contributions to the Study of the Function of Camphoric Acid.—A. Haller.—Not susceptible of useful abstraction.

Composition of Water, and on Gay-Lussac's Law of Volumes.—A. Leduc.—The author finds from his experiments, and from a comparison of the most recent determinations, the atomic weight of oxygen as 15.88, whilst its density with reference to hydrogen is 15.90. This result has a decided importance for the fixation of the atomic weights of the elementary bodies. The values given by Stas, *e.g.*, require to be multiplied by 0.995. The author finds in the comparison of these numbers a very remarkable confirmation of Gas-Lussac's law of volumes. The numbers hitherto admitted do not permit us to deduce the ponderal composition of gaseous compounds from their composition in volumes or reciprocally. Hitherto Gay-Lussac's law could only be regarded as an approximation. From what has been said it appears to be an exact law.

Nitrogenous Salts of Platinum.—M. Vèzes.—The author has previously described several chloronitrogenous, bromonitrogenous, and iodonitrogenous salts of potassium and platinum, of a composition intermediate between potassium platonitrite, $\text{Pt}(\text{NO}_2)_4\text{K}_2$, and the saturated haloid salt PtX_6K_4 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). He has since obtained several new salts of the same kind, and which, taken along with the former, constitute regular series. These compounds he now describes in their series.

Researches on the Sodium Pyrogallols.—M. de Forcrand.—A thermo-chemical paper not admitting of abstraction, and scarcely of sufficient interest to justify its insertion *in extenso*.

On Acetono-Resorcine.—H. Causse.—From the author's researches it results that acetone combines with resorcine to form an acetal. This compound, crystalline acetono-resorcine, results from the union of 2 mols. of

resorcin with 1 mol. of acetone, with elimination of 1 mol. of water. It contains only two free phenolic functions.

Utilisation of Burnt Pyrites for the Production of Salts of Iron.—A. and P. Buisine.—The authors mix roasted pyrites in fine powder with sulphuric acid at from 50° to 60° B. in sufficient quantity to saturate all the ferric oxide. The most suitable temperature is 300°. The sulphate thus obtained is a grey powder easy of packing and transport. Ferric chloride may be prepared by passing hydrochloric acid gas into a column filled with roasted pyrites. These ferric salts may be used in agriculture, in the purification of coal-gas, as a mordant in dyeing, as a precipitant for sewage, &c.

The Alterations of Chalybeate Waters.—F. Parmentier.—The author calls in question some of the results recently brought forward by M. Riban. He doubts the authenticity of M. Riban's samples, which were obtained at a "pharmacy." He does not consider the permanganate process suitable for the determination of iron under such circumstances.

On the Passage of Dissolved Substances through Mineral Filters and Capillary Tubes.—C. Chabridé.—The most important question is to know what happens if albuminous solutions are passed not through porous earth but simply through a very fine capillary tube. We observe first the passage of a solution less rich in albumen than the original solution, which becomes by degrees proportionally richer; then the passage of the solution thus concentrated is retarded, or perhaps a total stoppage of the flow if the percentage of albumen becomes too large.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 10.

Certain Properties of Manganese.—The chemical reactions of manganese as left by distillation from its amalgam have not been much studied. The metal thus obtained is pyrophoric, and decomposes certain of the most stable substances. In a current of carbon monoxide it burns with heat sufficient to raise the metal to white redness, and the decomposition of the gas is so rapid as to produce a partial vacuum in the apparatus. The action of carbon dioxide upon pyrophoric manganese is the same as that of carbon monoxide. Pyrophoric manganese reacts also upon gaseous sulphurous acid. With nitrogen dioxide and boron chloride there is also rapid absorption and great liberation of heat.

Action of Carbon Monoxide upon Iron.—M. Guntz.—Stammer, Deville, Lowthian Bell, and Schutzenberger observe that carbon monoxide is decomposed by iron, with deposition of carbon. Carbon monoxide, though very stable at high temperatures, is easily decomposed under the influence of oxidisable substances. If we take a pyrophoric iron obtained by igniting the oxalate, the action of carbon monoxide is the same, but less intense, as the metal has been reduced at a higher temperature. This reaction explains why in a certain zone of the blast furnace spongy iron meeting carbon monoxide is oxidised, yielding carbon and ferrous oxide, whilst in another zone this oxide is reduced by the carbon monoxide to yield iron and carbon dioxide, whilst finally, in passing into the hot zones of the furnace, the iron in contact with finely divided carbon is easily oxidised.

Analysis of Certain English Cheeses.—Dr. A. B. Griffiths.—Analyses of Stilton, Cheddar, Gloucester, Leicester, Cheshire, Cotherstone, Dorset, and Wiltshire cheeses. The two latter are poorest in fatty matter.

The Constitution of Milk.—L. Vaudin.—The author points out the very low degree of acidity in the milk of non-ruminant animals, which has hence been considered neutral or even alkaline. The milk of the ruminants is comparatively rich in acid and fluctuates little.

Amidonaphtholsulphonic Acids.—F. Reverdin and Ch. de la Harpe.—This lengthy memoir does not admit of useful abstraction.

Action of Acids upon Blood, and Formation of Oxyhæmoglobine by means of Hæmatine and Albumenoid Matter.—M. Bertin-Sans and J. Moitessier.—The authors have split up oxyhæmoglobine into hæmatine and albumenoid substance, and are now seeking to obtain synthetic hæmoglobine.

Transformation of Cupreine into Quinine and Homologous Bases.—E. Grimaux and E. Arnaud.—This paper also is not adapted for useful abridgment.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vii., No. 76.

The Deacon Process.—J. Kolb.—An elaborate discussion of the Deacon process in comparison with its rivals, especially the Weldon process. He considers that the Deacon process "has not said its last word." Its installation for an equal production is not appreciably more costly than the Weldon, and it requires less outlay for maintenance, for labour, and for fuel. The objection raised against it of yielding poor gases is not well founded. For anyone who has thoroughly studied the conditions of moisture and of temperature most favourable to the reaction, the problem of making a very rich chloride of lime with gases not containing more than 2 per cent of chlorine presents little difficulty. The future of the Deacon process is involved in that of the Leblanc process, and in the demand for sodium sulphate in the glass manufacture.

The Rodger Process for Melting Antimony.—From the *Journal of the Society of Chemical Industry*.

MISCELLANEOUS.

A Treatise on Manures.—Messrs. Whittaker and Co. have just issued a new edition of Dr. A. B. Griffiths's "Treatise on Manures." The present edition has been enlarged by fifty pages of new matter.

Specific Gravity of Silks.—Leo Vignon.—Already noticed. (We may mention it as an unfortunate circumstance that in France one and the same paper may be sent to two journals or be read before two societies without anything to show that each is not a distinct and independent document. This practice occasions waste of time and trouble to persons who wish to collate the literature of the subject.—*Bull. de la Soc. Chim. de Paris*, vii., No. 9.)

Apparatus for Determining the Temperature of Explosions.—S. Bein (*Zeit. Angew. Chemie*).—A double cylinder of sheet-iron supports in its conical neck an inserted test-tube containing a little sand. The test-tube is closed with a cork having two perforations through which pass a thermometer and a tube-funnel. When the temperature is near the explosion point, small portions of the substance in question are dropped in through the tube-funnel and explode on continued heating. The temperature is read off on the thermometer.

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. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

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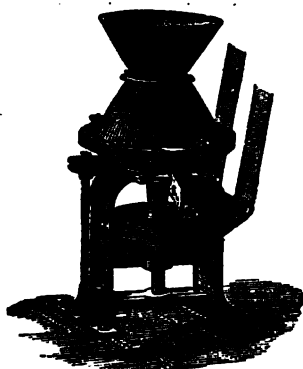
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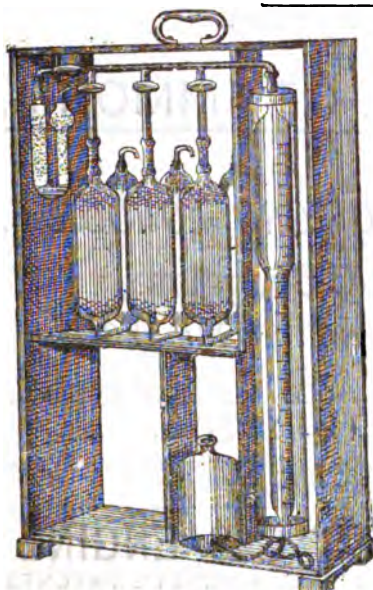
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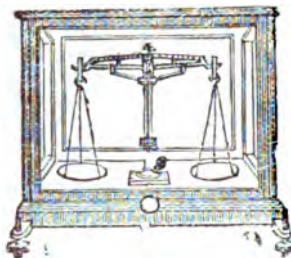
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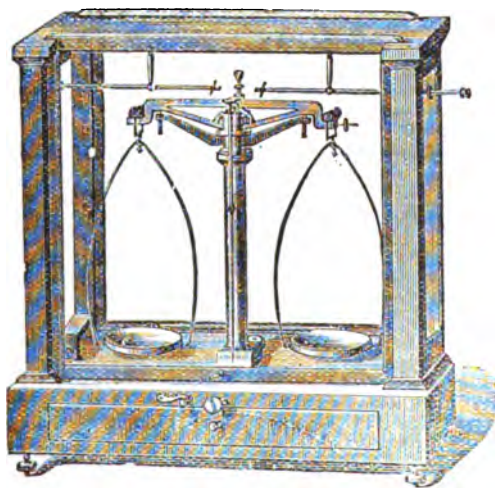


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BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

EDINBURGH, 1892.

INAUGURAL ADDRESS OF THE PRESIDENT,
SIR ARCHIBALD GEIKIE, LL.D., D.Sc.,
For. Sec. R.S., F.R.S.E., F.G.S., Director-General of
the Geological Survey of the United Kingdom.

IN its beneficent progress through these islands the British Association for the Advancement of Science now for the fourth time receives a welcome in this ancient capital. Once again, under the shadow of these antique towers, crowded memories of a romantic past fill our thoughts. The stormy annals of Scotland seem to move in procession before our eyes as we walk these streets, whose names and traditions have been made familiar to the civilised world by the genius of literature. At every turn, too, we are reminded, by the monuments which a grateful city has erected, that for many generations the pursuits which we are now assembled to foster have had their congenial home. Literature, philosophy, science, have each in turn been guided by the influence of the great masters who have lived here, and whose renown is the brightest gem in the chaplet around the brow of this "Queen of the North."

Lingering for a moment over these local associations, we shall find a peculiar appropriateness in the time of this renewed visit of the Association to Edinburgh. A hundred years ago a remarkable group of men was discussing here the great problem of the history of the earth. James Hutton, after many years of travel and reflection, had communicated to the Royal Society of this city, in the year 1785, the first outlines of his famous "Theory of the Earth." Among those with whom he took counsel in the elaboration of his doctrines were Black, the illustrious discoverer of "fixed air" and "latent heat"; Clerk, the sagacious inventor of the system of breaking the enemy's line in naval tactics; Hall, whose fertile ingenuity devised the first system of experiments in illustration of the structure and origin of rocks; and Playfair, through whose sympathetic enthusiasm and literary skill Hutton's views came ultimately to be understood and appreciated by the world at large. With these friends, so well able to comprehend and criticise his efforts to pierce the veil that shrouded the history of this globe, he paced the streets amid which we are now gathered together; with them he sought the crags and ravines around us, wherein Nature has laid open so many impressive records of her past; with them he sallied forth on those memorable expeditions to distant parts of Scotland, whence he returned laden with treasures from a field of observation which, though now so familiar, was then almost untrodden. The centenary of Hutton's "Theory of the Earth" is an event in the annals of science which seems most fittingly celebrated by a meeting of the British Association in Edinburgh.

In choosing from among the many subjects which might properly engage your attention on the present occasion, I have thought that it would not be inappropriate nor uninteresting to consider the more salient features of that "Theory," and to mark how much in certain departments of inquiry has sprung from the fruitful teaching of its author and his associates.

It was a fundamental doctrine of Hutton and his school that this globe has not always worn the aspect which it bears at present; that, on the contrary, proofs may everywhere be culled that the land which we now see has been formed out of the wreck of an older land. Among these proofs, the most obvious are supplied by some of the more familiar kinds of rock, which teach us that, though they are now portions of the dry land, they were originally sheets of gravel, sand, and mud, which had been worn from the face of long-vanished continents, and after being spread out over the floor of the sea were consolidated into compact stone, and were finally broken up and raised once more to form part of the dry land. This cycle of change involved two great systems of natural processes. On the one hand, men were taught that by the action of running water the materials of the solid land are in a state of continual decay and transport to the ocean. On the other hand, the ocean-floor is liable from time to time to be upheaved by some stupendous internal force akin to that which gives rise to the volcano and the earthquake. Hutton further perceived that not only had the consolidated materials been disrupted and elevated, but that masses of molten rock had been thrust upward among them, and had cooled and crystallised in large bodies of granite and other eruptive rocks which form so prominent a feature on the earth's surface.

It was a special characteristic of this philosophical system that it sought in the changes now in progress on the earth's surface an explanation of those which occurred in older times. Its founder refused to invent causes or modes of operation, for those with which he was familiar seemed to him adequate to solve the problems with which he attempted to deal. Nowhere was the profoundness of his insight more astonishing than in the clear, definite way in which he proclaimed and reiterated his doctrine, that every part of the surface of the continents, from mountain-top to sea-shore, is continually undergoing decay, and is thus slowly travelling to the sea. He saw that no sooner will the sea-floor be elevated into new land than it must necessarily become a prey to this universal and unceasing degradation. He perceived that, as the transport of disintegrated material is carried on chiefly by running water, rivers must slowly dig out for themselves the channels in which they flow, and thus that a system of valleys, radiating from the water-parting of a country, must necessarily result from the descent of the streams from the mountain-crests to the sea. He discerned that this ceaseless and widespread decay would eventually lead to the entire demolition of the dry land, but he contended that from time to time this catastrophe is prevented by the operation of the underground forces, whereby new continents are upheaved from the bed of the ocean. And thus in his system a due proportion is maintained between land and water, and the condition of the earth as a habitable globe is preserved.

A theory of the earth so simple in outline, so bold in conception, so full of suggestion, and resting on so broad a base of observation and reflection, ought, we might think, to have commanded at once the attention of men of science, even if it did not immediately awaken the interest of the outside world; but, as Playfair sorrowfully admitted, it attracted notice only very slowly, and several years elapsed before anyone showed himself publicly concerned about it, either as an enemy or a friend. Some of its earliest critics assailed it for what they asserted to be its irreligious tendency—an accusation which Hutton repudiated with much warmth. The sneer levelled by Cowper a few years earlier at all inquiries into the history of the universe was perfectly natural and intelligible from that poet's point of view. There was then a widespread belief that this world came into existence some six thousand years ago, and that any attempt greatly to increase that antiquity was meant as a blow to the authority of Holy Writ. So far, however, from aiming at the overthrow of orthodox beliefs, Hutton evidently regarded his "Theory" as an important con-

tribution in aid of natural religion. He dwelt with unfeigned pleasure on the multitude of proofs which he was able to accumulate of an orderly design in the operations of Nature, decay and renovation being so nicely balanced as to maintain the habitable condition of the planet. But as he refused to admit the predominance of violent action in terrestrial changes, and on the contrary contended for the efficacy of the quiet, continuous processes which we can even now see at work around us, he was constrained to require an unlimited duration of past time for the production of those revolutions of which he perceived such clear and abundant proofs in the crust of the earth. The general public, however, failed to comprehend that the doctrine of the high antiquity of the globe was not inconsistent with the comparatively recent appearance of man—a distinction which seems so obvious now.

Hutton died in 1797, beloved and regretted by the circle of friends who had learned to appreciate his estimable character and to admire his genius, but with little recognition from the world at large. Men knew not then that a great master had passed away from their midst, who had laid broad and deep the foundations of a new science; that his name would become a household word in after generations, and that pilgrims would come from distant lands to visit the scenes from which he drew his inspiration.

Many years might have elapsed before Hutton's teaching met with wide acceptance, had its recognition depended solely on his writings of the philosopher himself. For, despite his firm grasp of general principles and his mastery of the minutest details, he had acquired a literary style which, it must be admitted, was singularly unattractive. Fortunately for his fame, as well as for the cause of science, his devoted friend and disciple, Playfair, at once set himself to draw up an exposition of Hutton's views. After five years of labour on this task there appeared the classic "Illustrations of the Huttonian Theory," a work which for luminous treatment and graceful diction stands still without a rival in English geological literature. Though professing merely to set forth his friend's doctrines, Playfair's treatise was in many respects an original contribution to science of the highest value. It placed for the first time in the clearest light the whole philosophy of Hutton regarding the history of the earth, and enforced it with a wealth of reasoning and copiousness of illustration which obtained for it a wide appreciation. From long converse with Hutton, and from profound reflection himself, Playfair gained such a comprehension of the whole subject that, discarding the non-essential parts of his master's teaching, he was able to give so lucid and accurate an exposition of the general scheme of Nature's operations on the surface of the globe, that with only slight corrections and expansions his treatise may serve as a text-book to-day. In some respects, indeed, his volume was long in advance of its time. Only, for example, within the present generation has the truth of his teaching in regard to the origin of valleys been generally admitted.

Various causes contributed to retard the progress of the Huttonian doctrines. Especially potent was the influence of the teaching of Werner, who, though he perceived that a definite order of sequence could be recognised among the materials of the earth's crust, had formed singularly narrow conceptions of the great processes whereby that crust has been built up. His enthusiasm, however, fired his disciples with the zeal of proselytes, and they spread themselves over Europe to preach everywhere the artificial system which they had learnt in Saxony. By a curious fate Edinburgh became one of the great headquarters of Wernerism. The friends and followers of Hutton found themselves attacked in their own city by zealots who, proud of superior mineralogical acquirements, turned their most cherished ideas upside down, and assailed them in the uncouth jargon of Freiberg. Inasmuch as subterranean heat had

been invoked by Hutton as a force largely instrumental in consolidating and upheaving the ancient sediments that now form so great a part of the dry land, his followers were nicknamed Plutonists. On the other hand, as the agency of water was almost alone admitted by Werner, who believed the rocks of the earth's crust to have been chiefly chemical precipitates from a primeval universal ocean, those who adopted his views received the equally descriptive name of Neptunists. The battle of these two contending schools raged fiercely here for some years, and though mainly from the youth, zeal, and energy of Jameson, and the influence which his position as Professor in the University gave him, the Wernerian doctrines continued to hold their place, they were eventually abandoned even by Jameson himself, and the debt due to the memory of Hutton and Playfair was tardily acknowledged.

The pursuits and the quarrels of philosophers have from early times been a favourite subject of merriment to the outside world. Such a feud as that between the Plutonists and Neptunists would be sure to furnish abundant matter for the gratification of this propensity. Turning over the pages of Kay's "Portraits," where so much that was distinctive of Edinburgh society a hundred years ago is embalmed, we find Hutton's personal peculiarities and pursuits touched off in good-humoured caricature. In one plate he stands with arms folded and hammer in hand, meditating on the face of a cliff, from which rocky prominences in shape of human faces—perhaps grotesque likenesses of his scientific opponents—grin at him. In another engraving he sits in conclave with his friend Black, possibly arranging for that famous banquet of garden-snails which the two worthies had persuaded themselves to look upon as a strangely neglected form of human food. More than a generation later, when the Huttonists and Wernerists were at the height of their antagonism, the humorous side of the controversy did not escape the notice of the author of "Waverley," who, you will remember, when he makes Meg Dods recount the various kinds of wise folk brought by Lady Penelope Pennfeather from Edinburgh to St. Ronan's Well, does not forget to include those who "rin uphill and down dale, knapping the chucky-stanes to pieces wi' hammers, like sae mony road-makers run daft, to see how the world was made."

Among the names of the friends and followers of Hutton there is one which on this occasion deserves to be held in especial honour, that of Sir James Hall, of Dunglass. Having accompanied Hutton in some of his excursions, and having discussed with him the problems presented by the rocks of Scotland, Hall was familiar with the views of his master, and was able to supply him with fresh illustrations of them from different parts of the country. Gifted with remarkable originality and ingenuity, he soon perceived that some of the questions involved in the theory of the earth could probably be solved by direct physical experiment. Hutton, however, mistrusted any attempt "to judge of the great operations of Nature by merely kindling a fire and looking into the bottom of a little crucible." Out of deference to this prejudice Hall delayed to carry out his intention during Hutton's lifetime. But afterwards he instituted a remarkable series of researches which are memorable in the history of science as the first methodical endeavour to test the value of geological speculation by an appeal to actual experiment. The Neptunists, in ridiculing the Huttonian doctrine that basalt and similar rocks had once been molten, asserted that, had such been their origin, these masses would now be found in the condition of glass or slag. Hall, however, triumphantly vindicated his friend's view by proving that basalt could be fused, and thereafter by slow cooling could be made to resume a stony texture. Again, Hutton had asserted that under the vast pressures which must be effective deep within the earth's crust, chemical reactions must be powerfully influenced, and that under such conditions even limestone

may conceivably be melted without losing its carbonic acid. Various specious arguments had been adduced against this proposition, but by an ingeniously devised series of experiments Hall succeeded in converting limestone under great pressure into a kind of marble, and even fused it, and found that it then acted vigorously on other rocks. These admirable researches, which laid the foundations of experimental geology, constitute not the least memorable of the services rendered by the Huttonian school to the progress of science.

Clear as was the insight and sagacious the inferences of these great masters in regard to the history of the globe, their vision was necessarily limited by the comparatively narrow range of ascertained fact which up to their time had been established. They taught men to recognise that the present world is built of the ruins of an earlier one, and they explained with admirable perspicacity the operation of the processes whereby the degradation and renovation of land are brought about. But they never dreamed that a long and orderly series of such successive destructions and renewals had taken place, and had left their records in the crust of the earth. They never imagined that from these records it would be possible to establish a determinate chronology that could be read everywhere, and applied to the elucidation of the remotest quarter of the globe. It was by the memorable observations and generalisations of William Smith that this vast extension of our knowledge of the past history of the earth became possible. While the Scottish philosophers were building up their theory here, Smith was quietly ascertaining by extended journeys that the stratified rocks of the West of England occur in a definite sequence, and that each well-marked group of them can be discriminated from the others and identified across the country by means of its enclosed organic remains. It is nearly a hundred years since he made known his views, so that by a curious coincidence we may fitly celebrate on this occasion the centenary of William Smith as well as that of James Hutton. No single discovery has ever had a more momentous and far-reaching influence on the progress of a science than that law of organic succession which Smith established. At first it served merely to determine the order of the stratified rocks of England. But it soon proved to possess a world-wide value, for it was found to furnish the key to the structure of the whole stratified crust of the earth. It showed that within that crust lie the chronicles of a long history of plant and animal life upon this planet, it supplied the means of arranging the materials for this history in true chronological sequence, and it thus opened out a magnificent vista through a vast series of ages, each marked by its own distinctive types of organic life, which, in proportion to their antiquity, departed more and more from the aspect of the living world.

Thus a hundred years ago, by the brilliant theory of Hutton and the fruitful generalisation of Smith, the study of the earth received in our country the impetus which has given birth to the modern science of geology.

To review the marvellous progress which this science has made during the first century of its existence would require not one but many hours for adequate treatment. The march of discovery has advanced along a multitude of different paths, and the domains of Nature which have been included within the growing territories of human knowledge have been many and ample. Nevertheless, there are certain departments of investigation to which we may profitably restrict our attention on the present occasion, and wherein we may see how the leading principles that were proclaimed in this city a hundred years ago have germinated and borne fruit all over the world.

From the earliest times the natural features of the earth's surface have arrested the attention of mankind. The rugged mountain, the cleft ravine, the scarped cliff, the solitary boulder, have stimulated curiosity and prompted many a speculation as to their origin. The shells embedded by millions in the solid rocks of hills

far removed from the sea have still further pressed home these "obstinate questionings." But for many long centuries the advance of inquiry into such matters was arrested by the paramount influence of orthodox theology. It was not merely that the Church opposed itself to the simple and obvious interpretation of these natural phenomena. So implicit had faith become in the accepted views of the earth's age and of the history of creation, that even laymen of intelligence and learning set themselves unbidden and in perfect good faith to explain away the difficulties which Nature so persistently raised up, and to reconcile her teachings with those of the theologians. In the various theories thus originating, the amount of knowledge of natural law usually stood in inverse ratio to the share played in them by an uncontrolled imagination. The speculations, for example, of Burnet, Whiston, Whitehurst, and others in this country, cannot be read now without a smile. In no sense were they scientific researches; they can only be looked upon as exertations of learned ignorance. Springing mainly out of a laudable desire to promote what was believed to be the cause of true religion, they helped to retard inquiry, and exercised in that respect a baneful influence on intellectual progress.

It is the special glory of the Edinburgh school of geology to have cast aside all this fanciful trifling. Hutton boldly proclaimed that it was no part of his philosophy to account for the beginning of things. His concern lay only with the evidence furnished by the earth itself as to its origin. With the intuition of true genius he early perceived that the only solid basis from which to explore what has taken place in bygone time is a knowledge of what is taking place to-day. He thus founded his system upon a careful study of the processes whereby geological changes are now brought about. He felt assured that Nature must be consistent and uniform in her working, and that only in proportion as her operations at the present time are watched and understood will the ancient history of the earth become intelligible. Thus, in his hands, the investigation of the present became the key to the interpretation of the past. The establishment of this great truth was the first step towards the inauguration of a true science of the earth. The doctrine of the uniformity of causation in Nature became the fruitful principle on which the structure of modern geology could be built up.

Fresh life was now breathed into the study of the earth. A new spirit seemed to animate the advance along every pathway of inquiry. Facts that had long been familiar came to possess a wider and deeper meaning when their connection with each other was recognised as parts of one great harmonious system of continuous change. In no department of Nature, for example, was this broader vision more remarkably displayed than in that wherein the circulation of water between land and sea plays the most conspicuous part. From the earliest times men had watched the coming of clouds, the fall of rain, the flow of rivers, and had recognised that on this nicely adjusted machinery the beauty and fertility of the land depend. But they now learnt that this beauty and fertility involve a continual decay of the terrestrial surface; that the soil is a measure of this decay, and would cease to afford us maintenance were it not continually removed and renewed; that through the ceaseless transport of soil by rivers to the sea the face of the land is slowly lowered in level and carved into mountain and valley, and that the materials thus borne outwards to the floor of the ocean are not lost, but accumulate there to form rocks, which in the end will be upraised into new lands. Decay and renovation, in well-balanced proportions, were thus shown to be the system on which the existence of the earth as a habitable globe had been established. It was impossible to conceive that the economy of the planet could be maintained on any other basis. Without the circulation of water the life of plants and animals would be impossible, and with that circula-

tion the decay of the surface of the land and the renovation of its disintegrated materials are necessarily involved.

As it is now so must it have been in past time. Hutton and Playfair pointed to the stratified rocks of the earth's crust as demonstrations that the same processes which are at work to-day have been in operation from a remote antiquity. By thus placing their theory on a basis of actual observation, and providing in the study of existing operations a guide to the interpretation of those in past times, they rescued the investigation of the history of the earth from the speculations of theologians and cosmologists, and established a place for it among the recognised inductive sciences. To the guiding influence of their philosophical system the prodigious strides made by modern geology are in large measure to be attributed. And here in their own city, after the lapse of a hundred years, let us offer to their memory the grateful homage of all who have profited by their labours.

But while we recognise with admiration the far reaching influence of the doctrine of uniformity of causation in the investigation of the history of the earth, we must upon reflection admit that the doctrine has been pushed to an extreme perhaps not contemplated by its original founders. To take the existing conditions of Nature as a platform of actual knowledge from which to start in an inquiry into former conditions was logical and prudent. Obviously, however, human experience, in the few centuries during which attention has been turned to such subjects, has been too brief to warrant any dogmatic assumption that the various natural processes must have been carried on in the past with the same energy, and at the same rate as they are carried on now. Variations in energy might have been legitimately conceded as possible, though not to be allowed without reasonable proof in their favour. It was right to refuse to admit the operation of speculative causes of change when the phenomena were capable of natural and adequate explanation by reference to causes that can be watched and investigated. But it was an error to take for granted that no other kind of process or influence, nor any variation in the rate of activity save those of which man has had actual cognisance, has played a part in the terrestrial economy. The uniformitarian writers laid themselves open to the charge of maintaining a kind of perpetual motion in the machinery of Nature. They could find in the records of the earth's history no evidence of a beginning, no prospect of an end. They saw that many successive renovations and destructions had been effected on the earth's surface, and that this long line of vicissitudes formed a series of which the earliest were lost in antiquity, while the latest were still in progress towards an apparently illimitable future.

The discoveries of William Smith, had they been adequately understood, would have been seen to offer a corrective to this rigidly uniformitarian conception, for they revealed that the crust of the earth contains the long record of an unmistakable order of progression in organic types. They proved that plants and animals have varied widely in successive periods of the earth's history, the present condition of organic life being only the latest phase of a long preceding series, each stage of which recedes further from the existing aspect of things as we trace it backward into the past. And though no relic had yet been found, or indeed was ever likely to be found, of the first living things that appeared upon the earth's surface, the manifest simplification of types in the older formations pointed irresistibly to some beginning from which the long procession had taken its start. If then it could thus be demonstrated that there had been upon the globe an orderly march of living forms from the lowliest grades in early times to man himself to-day, and thus that in one department of her domain, extending through the greater portion of the records of the earth's history, Nature had not been uniform but had followed a vast and noble plan of evolution, surely it might have

been expected that those who discovered and made known this plan would seek to ascertain whether some analogous physical progression from a definite beginning might not be discernible in the framework of the globe itself.

But the early masters of the science laboured under two great disadvantages. In the first place, they found the oldest records of the earth's history so broken up and effaced as to be no longer legible. And in the second place, they lived under the spell of that strong reaction against speculation which followed the bitter controversy between the Neptunists and Plutonists in the earlier decades of the century. They considered themselves bound to search for facts, not to build up theories; and as in the crust of the earth they could find no facts which threw any light upon the primeval constitution and subsequent development of our planet, they shut their ears to any theoretical interpretations that might be offered from other departments of science. It was enough for them to maintain, as Hutton had done, that in the visible structure of the earth itself, no trace can be found of the beginning of things, and that the oldest terrestrial records reveal no physical conditions essentially different from those in which we still live. They doubtless listened with interest to the speculations of Kant, Laplace, and Herschel, on the probable evolution of nebulae, suns, and planets, but it was with the languid interest attaching to ideas that lay outside of their own domain of research. They recognised no practical connection between such speculations and the data furnished by the earth itself as to its own history and progress.

This curious lethargy with respect to theory on the part of men who were popularly regarded as among the most speculative followers of science would probably not have been speedily dispelled by any discovery made within their own field of observation. Even now, after many years of the most diligent research, the first chapters of our planet's history remain undiscovered or undecipherable. On the great terrestrial palimpsest, the earliest inscriptions seem to have been hopelessly effaced by those of later ages. But the question of the primeval condition and subsequent history of the planet might be considered from the side of astronomy and physics. And it was by investigations of this nature that the geological torpor was eventually dissipated. To our illustrious former president, Lord Kelvin, who occupied this chair when the Association last met in Edinburgh, is mainly due the rousing of attention to this subject. By the most convincing arguments he showed how impossible it was to believe in the extreme doctrine of uniformitarianism. And though, owing to uncertainty in regard to some of the data, wide limits of time were postulated by him, he insisted that within these limits the whole evolution of the earth and its inhabitants must have been comprised. While, therefore, the geological doctrine that the present order of Nature must be our guide to the interpretation of the past remained as true and fruitful as ever, it had now to be widened by the reception of evidence furnished by a study of the earth as a planetary body. The secular loss of heat, which demonstrably takes place both from the earth and the sun, made it quite certain that the present could not have been the original condition of the system. This diminution of temperature with all its consequences is not a mere matter of speculation, but a physical fact of the present time as much as any of the familiar physical agencies that affect the surface of the globe. It points with unmistakable directness to that beginning of things of which Hutton and his followers could find no sign.

Another modification or enlargement of the uniformitarian doctrine was brought about by continued investigation of the terrestrial crust and consequent increase of knowledge respecting the history of the earth. Though Hutton and Playfair believed in periodical catastrophes, and indeed required these to recur in order to renew and preserve the habitable condition of our planet, their

successors gradually came to view with repugnance any appeal to abnormal, and especially to violent manifestations of terrestrial vigour, and even persuaded themselves that such slow and comparatively feeble action as had been witnessed by man could alone be recognised in the evidence from which geological history must be compiled. Well do I remember in my own boyhood what a cardinal article of faith this prepossession had become. We were taught by our great and honoured master, Lyell, to believe implicitly in gentle and uniform operations, extended over indefinite periods of time, though possibly some, with the zeal of partisans, carried this belief to an extreme which Lyell himself did not approve. The most stupendous marks of terrestrial disturbance, such as the structure of great mountain chains, were deemed to be more satisfactorily accounted for by slow movements prolonged through indefinite ages than by any sudden convulsion.

What the more extreme members of the uniformitarian school failed to perceive was the absence of all evidence that terrestrial catastrophes, even on a colossal scale, might not be a part of the present economy of this globe. Such occurrences might never seriously affect the whole earth at one time, and might return at such wide intervals that no example of them has yet been chronicled by man. But that they have occurred again and again, and even within comparatively recent geological times, hardly admits of serious doubt. How far at different epochs and in various degrees they may have included the operation of cosmical influences lying wholly outside the planet, and how far they have resulted from movements within the body of the planet itself, must remain for further inquiry. Yet the admission that they have played a part in geological history may be freely made without impairing the real value of the Huttonian doctrine, that in the interpretation of this history our main guide must be a knowledge of the existing processes of terrestrial change.

As the most recent and best known of these great transformations, the Ice Age stands out conspicuously before us. If any one sixty years ago had ventured to affirm that at no very distant date the snows and glaciers of the Arctic regions stretched southwards into France, he would have been treated as a mere visionary theorist. Many of the facts to which he would have appealed in support of his statement were already well known, but they had received various other interpretations. By some observers, notably by Hutton's friend, Sir James Hall, they were believed to be due to violent debacles of water that swept over the face of the land. By others they were attributed to the strong tides and currents of the sea when the land stood at a lower level. The uniformitarian school of Lyell had no difficulty in elevating or depressing land to any required extent. Indeed, when we consider how averse these philosophers were to admit any kind or degree of natural operation other than those of which there was some human experience, we may well wonder at the boldness with which, on sometimes the slenderest evidence, they made land and sea change places, on the one hand submerging mountain ranges, and on the other placing great barriers of land where a deep ocean rolls. They took such liberties with geography because only well-established processes of change were invoked in the operations. Knowing that during the passage of an earthquake a territory bordering the sea may be upraised or sunk a few feet, they drew the sweeping inference that any amount of upheaval or depression of any part of the earth's surface might be claimed in explanation of geological problems. The progress of inquiry, while it has somewhat curtailed this geographical license, has now made known in great detail the strange story of the Ice Age.

There cannot be any doubt that after man had become a denizen of the earth, a great physical change came over the northern hemisphere. The climate, which had previously been so mild that evergreen trees flourished within ten or twelve degrees of the north pole, now be-

came so severe that vast sheets of snow and ice covered the north of Europe and crept southward beyond the south coast of Ireland, almost as far as the southern shores of England, and across the Baltic into France and Germany. This Arctic transformation was not an episode that lasted merely a few seasons, and left the land to resume thereafter its ancient aspect. With various successive fluctuations it must have endured for many thousands of years. When it began to disappear it probably faded away as slowly and imperceptibly as it had advanced, and when it finally vanished it left Europe and North America profoundly changed in the character alike of their scenery and of their inhabitants. The rugged rocky contours of earlier times were ground smooth and polished by the march of the ice across them, while the lower grounds were buried under wide and thick sheets of clay, gravel, and sand, left behind by the melting ice. The varied and abundant flora which had spread so far within the Arctic circle was driven away into more southern and less ungenial climes. But most memorable of all was the extirpation of the prominent large animals which, before the advent of the ice, had roamed over Europe. The lions, hyænas, wild horses, hippopotami, and other creatures either became entirely extinct or were driven into the Mediterranean basin and into Africa. In their place came northern forms—the reindeer, glutton, musk ox, woolly rhinoceros, and mammoth.

Such a marvellous transformation in climate, in scenery, in vegetation and in inhabitants, within what was after all but a brief portion of geological time, though it may have involved no sudden or violent convulsion, is surely entitled to rank as a catastrophe in the history of the globe. It was probably brought about mainly, if not entirely, by the operation of forces external to the earth. No similar calamity having befallen the continents within the time during which man has been recording his experience, the Ice Age might be cited as a contradiction to the doctrine of uniformity. And yet it manifestly arrived as part of the established order of Nature. Whether or not we grant that other ice ages preceded the last great one, we must admit that the conditions under which it arose, so far as we know them, might conceivably have occurred before and may occur again. The various agencies called into play by the extensive refrigeration of the northern hemisphere were not different from those with which we are familiar. Snow fell and glaciers crept as they do to-day. Ice scored and polished rocks exactly as it still does among the Alps and in Norway. There was nothing abnormal in the phenomena save the scale on which they were manifested. And thus, taking a broad view of the whole subject, we recognise the catastrophe, while at the same time we see in its progress the operation of those same natural processes which we know to be integral parts of the machinery whereby the surface of the earth is continually transformed.

Among the debts which science owes to the Huttonian school, not the least memorable is the promulgation of the first well-founded conceptions of the high antiquity of the globe. Some six thousand years had previously been believed to comprise the whole life of the planet, and indeed of the entire universe. When the curtain was then first raised that had veiled the history of the earth, and men, looking beyond the brief span within which they had supposed that history to have been transacted, beheld the records of a long vista of ages stretching far away into a dim illimitable past, the prospect vividly impressed their imagination. Astronomy had made known the immeasurable fields of space; the new science of geology seemed now to reveal boundless distances of time. The more the terrestrial chronicles were studied the farther could the eye range into an antiquity so vast as to defy all attempts to measure or define it. The progress of research continually furnished additional evidence of the enormous duration of the ages that preceded the coming of man, while, as knowledge

increased, periods that were thought to have followed each other consecutively were found to have been separated by prolonged intervals of time. Thus the idea arose and gained universal acceptance that, just as no boundary could be set to the astronomer in his free range through space, so the whole of bygone eternity lay open to the requirements of the geologist. Playfair, re-echoing and expanding Hutton's language, had declared that neither among the records of the earth nor in the planetary motions can any trace be discovered of the beginning or of the end of the present order of things; that no symptom of infancy or of old age has been allowed to appear on the face of Nature, nor any sign by which either the past or the future duration of the universe can be estimated; and that although the Creator may put an end, as He no doubt gave a beginning, to the present system, such a catastrophe will not be brought about by any of the laws now existing, and is not indicated by anything which we perceive. This doctrine was naturally espoused with warmth by the extreme uniformitarian school, which required an unlimited duration of time for the accomplishment of such slow and quiet cycles of change as they conceived to be alone recognisable in the records of the earth's past history.

It was Lord Kelvin who, in the writings to which I have already referred, first called attention to the fundamentally erroneous nature of these conceptions. He pointed out that, from the high internal temperature of our globe, increasing inwards as it does, and from the rate of loss of its heat, a limit may be fixed to the planet's antiquity. He showed that, so far from there being no sign of a beginning, and no prospect of an end to the present economy, every lineament of the solar system bears witness to a gradual dissipation of energy from some definite starting-point. No very precise data were then, or indeed are now, available for computing the interval which has elapsed since that remote commencement, but he estimated that the surface of the globe could not have consolidated less than twenty millions of years ago, for the rate of increase of temperature inwards would in that case have been higher than it actually is; nor more than 400 millions of years ago, for then there would have been no sensible increase at all. He was inclined, when first dealing with the subject, to believe that, from a review of all the evidence then available, some such period as 100 millions of years would embrace the whole geological history of the globe.

It is not a pleasant experience to discover that a fortune which one has unconcernedly believed to be ample has somehow taken to itself wings and disappeared. When the geologist was suddenly awakened by the energetic warning of the physicist, who assured him that he had enormously overdrawn his account with past time, it was but natural under the circumstances that he should think the accountant to be mistaken, who thus returned to him dishonoured the large drafts he had made on eternity. He saw how wide were the limits of time deducible from physical considerations, how vague the data from which they had been calculated. And though he could not help admitting that a limit must be fixed beyond which his chronology could not be extended, he consoled himself with the reflection that after all a hundred millions of years was a tolerably ample period of time, and might possibly have been quite sufficient for the transaction of all the prolonged sequence of events recorded in the crust of the earth. He was therefore disposed to acquiesce in the limitation thus imposed upon geological history.

But physical inquiry continued to be pushed forward with regard to the early history and the antiquity of the earth. Further consideration of the influence of tidal friction in retarding the earth's rotation, and of the sun's rate of cooling, led to sweeping reductions of the time allowable for the evolution of the planet. The geologist found himself in the plight of Lear when his bodyguard of one hundred knights was cut down. "What need

you five-and-twenty, ten or five?" demands the inexorable physicist, as he remorselessly strikes slice after slice from his allowance of geological time. Lord Kelvin is willing, I believe, to grant us some twenty millions of years, but Professor Tate would have us content with less than ten millions.

In scientific as in other mundane questions there may often be two sides, and the truth may ultimately be found not to lie wholly with either. I frankly confess that the demands of the early geologists for an unlimited series of ages were extravagant, and even, for their own purposes, unnecessary, and that the physicist did good service in reducing them. It may also be freely admitted that the latest conclusions from physical considerations of the extent of geological time require that the interpretation given to the record of the rocks should be rigorously revised with the view of ascertaining how far that interpretation may be capable of modification or amendment. But we must also remember that the geological record constitutes a voluminous body of evidence regarding the earth's history which cannot be ignored, and must be explained in accordance with ascertained natural laws. If the conclusions derived from the most careful study of this record cannot be reconciled with those drawn from physical considerations, it is surely not too much to ask that the latter should be also revised. It has been well said that the mathematical mill is an admirable piece of machinery, but that the value of what it yields depends upon the quality of what is put into it. That there must be some flaw in the physical argument I can, for my own part, hardly doubt, though I do not pretend to be able to say where it is to be found. Some assumption, it seems to me, has been made, or some consideration has been left out of sight, which will eventually be seen to vitiate the conclusions, and which when duly taken into account will allow time enough for any reasonable interpretation of the geological record.

In problems of this nature, where geological data capable of numerical statement are so needful, it is hardly possible to obtain trustworthy computations of time. We can only measure the rate of changes in progress now, and infer from these changes the length of time required for the completion of results achieved by the same processes in the past. There is fortunately one great cycle of movement which admits of careful investigation, and which has been made to furnish valuable materials for estimates of this kind. The universal degradation of the land, so notable a characteristic of the earth's surface, has been regarded as an extremely slow process. Though it goes on without ceasing, yet from century to century it seems to leave hardly any perceptible trace on the landscapes of a country. Mountains and plains, hills and valleys, appear to wear the same familiar aspect which is indicated in the oldest pages of history. This obvious slowness in one of the most important departments of geological activity doubtless contributed in large measure to form and foster a vague belief in the vastness of the antiquity required for the evolution of the earth.

But, as geologists eventually came to perceive, the rate of degradation of the land is capable of actual measurement. The amount of material worn away from the surface of any drainage-basin and carried in the form of mud, sand, or gravel by the main river into the sea, represents the extent to which that surface has been lowered by waste in any given period of time. But denudation and deposition must be equivalent to each other. As much materials must be laid down in sedimentary accumulations as has been mechanically removed, so that in measuring the annual bulk of sediment borne into the sea by a river, we obtain a clue not only to the rate of denudation of the land, but also to the rate at which the deposition of new sedimentary formations takes place.

As might be expected, the activities involved in the lowering of the surface of the land are not everywhere equally energetic. They are naturally more vigorous

where the rainfall is heavy, where the daily range of temperature is large, and where frosts are severe. Hence they are obviously much more effective in mountainous regions than on plains; and their results must constantly vary, not only in different basins of drainage, but even, and sometimes widely, within the same basin. Actual measurement of the proportion of sediment in riverwater shows that while in some cases the lowering of the surface of the land may be as much as 1-730th of a foot in a year, in others it falls as low as 1-6800. In other words, the rate of deposition of new sedimentary formations, over an area of sea-floor equivalent to that which has yielded the sediment, may vary from one foot in 730 years to one foot in 6800 years.

If now we take these results and apply them as measures of the length of time required for the deposition of the various sedimentary masses that form the outer part of the earth's crust, we obtain some indication of the duration of geological history. On a reasonable computation these stratified masses, where most fully developed, attain a united thickness of not less than 100,000 feet. If they were all laid down at the most rapid recorded rate of denudation, they would require a period of seventy-three millions of years for their completion. If they were laid down at the slowest rate they would demand a period of not less than 680 millions.

But it may be argued that all kinds of terrestrial energy are growing feeble, that the most active denudation now in progress is much less vigorous than that of bygone ages, and hence that the stratified part of the earth's crust may have been put together in a much briefer space of time than modern events might lead us to suppose. Such arguments are easily adduced and look sufficiently specious, but no confirmation of them can be gathered from the rocks. On the contrary, no one can thoughtfully study the various systems of stratified formations without being impressed by the fulness of their evidence that, on the whole, the accumulation of sediment has been extremely slow. Again and again we encounter groups of strata composed of thin paper-like laminæ of the finest silt, which evidently settled down quietly and at intervals on the sea bottom. We find successive layers covered with ripple marks and sun cracks, and we recognise in them memorials of ancient shores where sand and mud tranquilly gathered as they do in sheltered estuaries at the present day. We can see no proof whatever, nor even any evidence which suggests, that on the whole the rate of waste and sedimentation was more rapid during Mesozoic and Palæozoic time than it is to-day. Had there been any marked difference in this rate from ancient to modern times, it would be incredible that no clear proof of it should have been recorded in the crust of the earth.

But in actual fact the testimony in favour of the slow accumulation and high antiquity of the geological record is much stronger than might be inferred from the mere thickness of the stratified formations. These sedimentary deposits have not been laid down in one unbroken sequence, but have had their continuity interrupted again and again by upheaval and depression. So fragmentary are they in some regions that we can easily demonstrate the length of time represented there by still existing sedimentary strata to be vastly less than the time indicated by the gaps in the series.

There is yet a further and impressive body of evidence furnished by the successive races of plants and animals which have lived upon the earth and have left their remains sealed up within its rocky crust. No one now believes in the exploded doctrine that successive creations and universal destructions of organic life are chronicled in the stratified rocks. It is everywhere admitted that from the remotest times up to the present day there has been an onward march of development, type succeeding type in one long continuous progression. As to the rate of this evolution, precise data are wanting. There is, however, the important negative argument furnished by

the absence of evidence of recognisable specific variations of organic forms since man began to observe and record. We know that within human experience a few species have become extinct, but there is no conclusive proof that a single new species has come into existence, nor are appreciable variations readily apparent in forms that live in a wild state. The seeds and plants found with Egyptian mummies, and the flowers and fruits depicted on Egyptian tombs, are easily identified with the vegetation of modern Egypt. The embalmed bodies of animals found in that country show no sensible divergence from the structure or proportions of the same animals at the present day. The human races of Northern Africa and Western Asia were already as distinct when portrayed by the ancient Egyptian artists as they are now, and they do not seem to have undergone any perceptible change since then. Thus a lapse of four or five thousand years has not been accompanied by any recognisable variation in such forms of plant and animal life as can be tendered in evidence. Absence of sensible change in these instances is, of course, no proof that considerable alteration may not have been accomplished in other forms more exposed to vicissitudes of climate and other external influences. But it furnishes at least a presumption in favour of the extremely tardy progress of organic variation.

If, however, we extend our vision beyond the narrow range of human history, and look at the remains of the plants and animals preserved in those younger formations which, though recent when regarded as parts of the whole geological record, must be many thousands of years older than the very oldest of human monuments, we encounter the most impressive proofs of the persistence of specific forms. Shells which lived in our seas before the coming of the Ice Age present the very same peculiarities of form, structure, and ornament which their descendants still possess. The lapse of so enormous an interval of time has not sufficed seriously to modify them. So, too, with the plants and the higher animals which still survive. Some forms have become extinct, but few or none which remain display any transitional gradations into new species. We must admit that such transitions have occurred, that indeed they have been in progress ever since organised existence began upon our planet, and are doubtless taking place now. But we cannot detect them on the way, and we feel constrained to believe that their march must be excessively slow.

There is no reason to think that the rate of organic evolution has ever seriously varied; at least no proof has been adduced of such variation. Taken in connection with the testimony of the sedimentary rocks, the inferences deducible from fossils entirely bear out the opinion that the building up of the stratified crust of the earth has been extremely gradual. If the many thousands of years which have elapsed since the Ice Age have produced no appreciable modification of surviving plants and animals, how vast a period must have been required for that marvellous scheme of organic development which is chronicled in the rocks!

After careful reflection on the subject, I affirm that the geological record furnishes a mass of evidence which no arguments drawn from other departments of Nature can explain away, and which, it seems to me, cannot be satisfactorily interpreted save with an allowance of time much beyond the narrow limits which recent physical speculation would concede.

I have reserved for final consideration a branch of the history of the earth which, while it has become, within the lifetime of the present generation, one of the most interesting and fascinating departments of geological inquiry, owed its first impulse to the far-seeing intellects of Hutton and Playfair. With the penetration of genius these illustrious teachers perceived that if the broad masses of land and the great chains of mountains owe their origin to stupendous movements which from time to time have convulsed the earth, their details of contour must

be mainly due to the eroding power of running water. They recognised that as the surface of the land is continually worn down, it is essentially by a process of sculpture that the physiognomy of every country has been developed, valleys being hollowed out and hills left standing, and that these inequalities in topographical detail are only varying and local accidents in the progress of the one great process of the degradation of the land.

From the broad and guiding outlines of theory thus sketched we have now advanced amid ever-widening multiplicity of detail into a fuller and nobler conception of the origin of scenery. The law of evolution is written as legibly on the landscapes of the earth as on any other page of the Book of Nature. Not only do we recognise that the existing topography of the continents, instead of being primeval in origin, has gradually been developed after many precedent mutations, but we are enabled to trace these earlier revolutions in the structure of every hill and glen. Each mountain-chain is thus found to be a memorial of many successive stages in geographical evolution. Within certain limits, land and sea have changed places again and again. Volcanoes have broken out and have become extinct in many countries long before the advent of man. Whole tribes of plants and animals have meanwhile come and gone, and in leaving their remains behind them as monuments at once of the slow development of organic types, and of the prolonged vicissitudes of the terrestrial surface, have furnished materials for a chronological arrangement of the earth's topographical features. Nor is it only from the organisms of former epochs that broad generalisations may be drawn regarding revolutions in geography. The living plants and animals of to-day have been discovered to be eloquent of ancient geographical features that have long since vanished. In their distribution they tell us that climates have changed, that islands have been disjoined from continents, that oceans once united have been divided from each other, or once separate have now been joined; that some tracts of land have disappeared, while others for prolonged periods of time have remained in isolation. The present and the past are thus linked together not merely by dead matter, but by the world of living things, into one vast system of continuous progression.

In this marvellous increase of knowledge regarding the transformations of the earth's surface, one of the most impressive features, to my mind, is the power now given to us of perceiving the many striking contrasts between the present and former aspects of topography and scenery. We seem to be endowed with a new sense. What is seen by the bodily eye—mountain, valley, or plain—serves but as a veil, beyond which, as we raise it, visions of long-lost lands and seas rise before us in a far-retreating vista. Pictures of the most diverse and opposite character are beheld, as it were, through each other, their lineaments subtly interwoven and even their most vivid contrasts subdued into one blended harmony. Like the poet, "we see, but not by sight alone"; and the "ray of fancy" which, as a sunbeam, lightened up his landscape, is for us broadened and brightened by that play of the imagination which science can so vividly excite and prolong.

Admirable illustrations of this modern interpretation of scenery are supplied by the district wherein we are now assembled. On every side of us rise the most convincing proofs of the reality and potency of that ceaseless sculpture by which the elements of landscape have been carved into their present shapes. Turn where we may, our eyes rest on hills that project above the lowland, not because they have been upheaved into these positions, but because their stubborn materials have enabled them better to withstand the degradation which has worn down the softer strata into the plains around them. Inch by inch the surface of the land has been lowered, and each hard rock successively laid bare has communicated its own characteristics of form and colour to the scenery.

If, standing on the Castle Rock, the central and oldest site in Edinburgh, we allow the bodily eye to wander over the fair landscape, and the mental vision to range through the long vista of earlier landscapes which science here reveals to us, what a strange series of pictures passes before our gaze! The busy streets of to-day seem to fade away into the mingled copsewood and forest of prehistoric time. Lakes that have long since vanished gleam through the woodlands, and a rude canoe pushing from the shore startles the red deer that had come to drink. While we look, the picture changes to a polar scene, with bushes of stunted Arctic willow and birch, among which herds of reindeer browse and the huge mammoth makes his home. Thick sheets of snow are draped all over the hills around, and far to the north-west the distant gleam of glaciers and snow-fields marks the line of the Highland mountains. As we muse on this strange contrast to the living world of to-day the scene appears to grow more Arctic in aspect, until every hill is buried under one vast sheet of ice, 2000 feet or more in thickness, which fills up the whole midland valley of Scotland and creeps slowly eastward into the basin of the North Sea. Here the curtain drops upon our moving pageant, for in the geological record of this part of the country an enormous gap occurs before the coming of the Ice Age.

When once more the spectacle resumes its movement the scene is found to have utterly changed. The familiar hills and valleys of the Lothians have disappeared. Dense jungles of a strange vegetation—tall reeds, club-mosses, and tree-ferns—spread over the steaming swamps that stretch for leagues in all directions. Broad lagoons and open seas are dotted with little volcanic cones which throw out their streams of lava and showers of ashes. Beyond these, in dimmer outline and older in date, we descry a wide lake or inland sea, covering the whole midland valley and marked with long lines of active volcanoes, some of them several thousand feet in height. And still further and fainter over the same region, we may catch a glimpse of that still earlier expanse of sea which in Silurian times overspread most of Britain. But beyond this scene our vision fails. We have reached the limit across which no geological evidence exists to lead the imagination into the primeval darkness beyond.

Such in briefest outline is the succession of mental pictures which modern science enables us to frame out of the landscapes around Edinburgh. They may be taken as illustrations of what may be drawn, and sometimes with even greater fullness and vividness, from any district in these islands. But I cite them especially because of their local interest in connection with the present meeting of the Association, and because the rocks that yield them gave inspiration to those great masters whose claims on our recollection, not least for their explanation of the origin of scenery, I have tried to recount this evening. But I am further impelled to dwell on these scenes from an overmastering personal feeling to which I trust I may be permitted to give expression. It was these green hills and grey crags that gave me in boyhood the impulse that has furnished the work and joy of my life. To them, amid changes of scene and surroundings, my heart ever fondly turns, and here I desire gratefully to acknowledge that it is to their influence that I am indebted for any claim I may possess to stand in the proud position in which your choice has placed me.

Hydrogen Sulphide Free from Arsenic.—H. Habermann (*Chemiker Zeitung*).—The author mixes 1 part by weight of calcium sulphide and 2 parts crystallised magnesium chloride with as much water as will form a thin paste, and warms at first gently and afterwards more strongly. Habermann has also proposed to free hydrogen sulphide from traces of arsenic by a passage over iodine, and then through water in a washing-bottle. He proposes a similar treatment for purifying hydrogen from hydrogen arsenide, phosphide, and sulphide.

NEW METHOD OF PRODUCING GEMS ARTIFICIALLY.

By JAMES MORRIS.

It has been claimed by a French *savant* that chemistry is a French science. While this very broad claim cannot be conceded in its entirety, it may well be admitted that the production of gems artificially is a French domain, and that the Paris specialists have up till now led the way in this field of research and synthesis. In how far the French, or any other methods, are the methods of nature, can be determined only by further experiment, and by study of, and comparison with, natural phenomena. It is at least likely that the most natural method will be the most successful one in practice.

In his large work on mineralogy, Quenstedt remarks in connection with the experiments of Senarmont on the artificial production of quartz, "Allein dennoch bleibt noch Natur unsere Lehrmeisterin."

It is a curious fact that many of the most valuable gems are found in nature together, and it almost seems as if in the chemistry of the earth's crust a few generic processes had determined the formation of groups of crystals, both of the noble class and of the more ordinary kinds.

This rule is sometimes so marked that the presence of one crystal is almost a sure indication that a certain other crystal is not far away. Thus, in the diamond fields of Brazil crystals of anatase accompanied the diamonds, as a slave his master, and were thus termed by the Spaniards "captivos."

Although I am not yet in a position to publish the method of production which I follow, it may for the present be stated that the process is a simple one, and that at least many analogies point to the probability of its being one of the natural and generic processes referred to above.

The bulk of the products consist of rounded and compact crystals, composed entirely or chiefly of alumina. Individuals have been formed over one-sixteenth of an inch in diameter, and others approaching that size in very large numbers. The most of them are transparent, and by subsequent prolonged ignition with nitrate of cobalt, followed by heating in acid, some were found to have taken on the blue colour. Other tests were also applied. They were very hard, and I believe that I am justified, in a mineralogical sense, in calling the transparent crystals colourless sapphires.

In future experiments the colouring-matters will be added at an early stage of the process. They contain little or no silica. The crystals act in varying degrees on polarised light, and there are specimens which remain quite dark on revolution between the prisms.

It is not impossible that these latter are spinels, but many things point to at least some of them being diamonds. They are smaller, and much fewer in number than the chief product, and I have not yet exposed any of them individually to destructive tests. It is a case in which chemical analysis, applied to the crystals *en masse*, is not sufficient.

The sparkle of some of these small crystals is magnificent. Carbon was present in the production of all the crystals, and some of the aluminous ones contain a little of that element. C. Greville Williams found a small amount of carbon in beryls and emeralds. Luzy has recently shown that carbon is directly soluble in fused mineral matter.

It is a curious fact that in the "pipes" in South Africa garnets and other more or less noble crystals accompany the diamond. Had less silica been present it is not unlikely that rubies and sapphires would also have been formed. The manner in which some of my products cut glass is remarkable. They do not merely furrow it, but produce a deep fracture, very suggestive of diamond, or of some body containing carbon in the diamond form.

The noble nature of the crystals is beyond doubt. Some which I have tested are more infusible than platinum. I have specimens half embedded in the platinum which had been fused. The crystals showed merely slight softening. On prolonged ignition at a somewhat lower, but still very high, temperature, they became coated with microscopic crystals of platinum. Some of these were thin, hexagonal plates of wonderful beauty.

Mr. Joly, of Dublin, was perhaps the first to bring prominently before chemists the considerable volatility of platinum, even under its melting-point. He obtained similar crystals on strongly igniting fragments of quartz on his platinum ribbon.

Among the tests used to indicate the presence of carbon in the aluminous crystals, the following ocular proof is very strong. Some of the crystals were fused in borax in a small platinum capsule. In the fused mass there remained a few skeletal forms having a cokey appearance. This cokey matter was afterwards treated with fluoride of ammonium and with acid. It was neither dissolved nor even dimmed. Silica in such a physical condition would have disappeared.

The evident presence of carbon in some of the products makes the likelihood of the small, singly refractive crystals, being not spinels, but diamonds, all the greater.

I hope to be able, at a not too distant date, to say something about the genesis of the crystals, and to communicate the results of further investigation. I shall also try to arrange some differential experiments for the purpose of increasing the amount of carbon in the crystals, both collectively and individually.

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CAN ARSENIC BE QUANTITATIVELY VOLATILISED AS ARSENIC HYDRIDE?*

By F. W. SCHMIDT.

THE question whether arsenic can be quantitatively volatilised as arseniuretted hydrogen has often been discussed. It was natural to utilise the beautiful reaction for quantitative determinations in which arseniuretted hydrogen in contact with a dilute solution of silver is transformed into arsenious acid and metallic silver. But in by far the most cases the researches undertaken for this purpose have led to no result, since it was not found practicable to convert entirely either arsenic or antimony into volatile hydrogen compounds, though we find in literature indications that this has been effected in certain cases, especially when the quantities of arsenic were only small. Still no decisive conclusion was reached, and Fresenius pronounces a severe condemnation (*Lehrbuch der Quantitativen Analyse*, vol. i., 641), on all gravimetric processes founded upon the volatility of arseniuretted and antimoniuiretted hydrogen.

If I felt induced to resume experiments in this direction it was because an observation had shown that the entire arsenic present in commercial zinc-powder could be volatilised as arseniuretted hydrogen on treatment with hydrochloric acid. The following method was therefore adopted.

In the first place the accuracy of the above mentioned observation had to be quantitatively confirmed. 10 grms. of commercial zinc-powder were carefully dissolved in concentrated nitric acid (concentrated acid was used to prevent the volatilisation of traces of arsenic), the nitric acid present was expelled by evaporating down the solution obtained on the water-bath along with concentrated hydrochloric acid, and after reducing the arsenic acid by means of ferrous chloride the arsenic was distilled over as $AsCl_3$, according to E. Fischer's process. The arsenic

* *Zeit. Anorganische Chemie.*

was then determined in the distillate as trisulphide in the ordinary manner, whence it appeared that the commercial zinc-powder contained 0.04 per cent of metallic arsenic. As a check, a second portion of 10 grms. of the zinc-powder was submitted to the same operation, the AsCl_3 driven over on the addition of an excess of ferrous chloride, the distillate supersaturated with sodium bicarbonate, and the arsenic titrated by means of decinormal solution of iodine; the 1.16 c.c. of the solution consumed represented in the same manner 0.04 per cent of metallic arsenic.

As the proportion of arsenic in the zinc-powder was thus established, I could proceed to the determination of the arsenic in the form of arseniuretted hydrogen. The apparatus used for this purpose consisted of a round flask of the capacity of 200 c.c., fitted with a dropping funnel and a gas-delivery tube leading to three absorbent vessels each holding 100 c.c. The flask is placed upon a water-bath so that the reaction may be assisted by heat. The distance of the first absorption vessel from the round flask is at least 20 c.m., so that the liquid in the former may not become heated. The first absorption vessel is half filled with a solution of silver of the concentration 1:50; the second contains silver solution of the concentration 1:10, and the third contains bromohydrochloric acid. Ten grms. of the commercial zinc-powder were weighed into the round flask; the substance was moistened through with water, the apparatus is connected together, and hydrochloric acid (1 vol. concentrated acid diluted with 1 vol. water), is gradually introduced by the dropping funnel. The gas liberated at once deposited black metallic silver in the first absorption vessel. As soon as the escape of gas became sluggish the flame was lighted beneath the water-bath, and when the zinc-powder was fully dissolved a slow current of hydrogen previously washed in silver solution (1:10), and consequently free from arsenic, was passed through the apparatus for about half an hour so as to sweep the last traces of arseniuretted hydrogen out of the round flask. The contents of the third absorption vessel, and the liquid in the round flask, were found on careful examination utterly free from arsenic; all the arsenic, therefore, as in the first observation, had been volatilised as a hydrogen compound, and at the same time the transformation of the arseniuretted hydrogen with the silver solution was completed in the second absorption vessel, so that the third contained not a trace of arsenic. From the contents of the first and second absorbent vessel, the excess of silver was separated by means of sodium chloride, and the arsenic in the filtrate from the silver chloride, after an addition of sodium bicarbonate, was titrated with decinormal solution of iodine. There were again used, until a blue colour appeared, 1.16 c.c. of the standard solution corresponding to 0.04 per cent of metallic arsenic in the commercial zinc powder.

This result rendered it very probable that the complete volatilisation of the arsenic from the zinc powder in the state of arseniuretted hydrogen depends on the presence of the arsenic in the zinc powder as a zinc arsenide, or else in an exceedingly finely divided metallic state which energetically assists the quantitative conversion of the arsenic into its hydrogen compound. A quantitative volatilisation must therefore be attainable also in other cases if the arsenic is converted into a state analogous to combination or to fine metallic sub-division.

(To be continued).

A Closure for Burettes without a Cock.—Dannbacher (*Pharm. Central Halle*).—The arrangement consists of two perforated plates of wood rather elevated at the margin and fixed upon the ends of the burette and the outflow tube, both previously covered with a caoutchouc tube. When fixing the wooden plates the flexible tube receives a slight tension, which suffices to press the wooden plates against each other, so that after any rotation they remain as they have last been placed.

METHODS OF SUGAR ANALYSIS.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

(Continued from p. 60).

II.—The Syrup to be Examined may Contain Starch Sugar.

In this case a direct polarisation must first be made. If this gives a coefficient of purity above 70, further examination is unnecessary, as it would only tend to raise the coefficient, never to lower it.

If, however, the coefficient falls below 70, the presence of starch sugar is still possible. To determine whether any is present the syrup is inverted as in I., and made up to the mark.

It is then decolourised by adding $\frac{1}{2}$ to 1; in the case of dark syrups from 2 to 3 grms. of bone charcoal previously washed with hydrochloric acid or of charred blood. If the latter is used, its absorption factor for invert sugar must be previously determined, and a corresponding correction in the polarimetric reading made in case the left-handed rotation is to be estimated accurately. In the present case it is sufficient to approximately determine this rotation at about 20°. Experience has shown that unadulterated syrups do not always have a *lævo*-rotation corresponding to 0.33 of the original right-handed rotation, but in all cases it is at least one-fifth of the original reading. A syrup polarising 55 directly should, after inversion, read at least -11, calculated for normal weight. If this syrup should read -10 or less, or should even rotate to the right, then it has been adulterated with starch sugar. When the absence of starch sugar has thus been proved, the syrup must be examined according to I.

If, however, starch-sugar is present, then we must arrive at the total sucrose by adding to the direct polarisation the invert sugar found by Fehling's solution. In this procedure the Fehling's solution is used according to Soxhlet's directions, but as the amount of solution taken by this author would not suffice for 10 grms. of substance, we have to make preliminary experiments to determine the quantity of syrup which should be taken. This is done most easily by diluting 10 grms. syrup to 100 c.c., placing 5 c.c. of Fehling's solution into several test-tubes, and adding successively 8, 6, 4, and 2 c.c. of the syrup solution. Upon boiling we will arrive at a point where the Fehling's solution is no longer decolourised. If this is the case with 6 c.c., then 6 grms. of substance are weighed out, dissolved in 50 c.c. of water, and 50 c.c. of Fehling's solution added. The whole is boiled for two minutes, and the analysis conducted as in the estimation of invert sugar.

The invert sugar is calculated according to Meissl's table. The following data concerning the use of the table are taken from the original article, "*Zeitschrift des Vereins für die Rübenzuckerindustrie des Deutschen Reiches*," 1883, p. 768:—

Let—

$$\text{I. } \frac{\text{Cu}}{2} = \text{approximate absolute amount invert sugar} = Z.$$

$$\text{II. } Z \times \frac{100}{p} = \text{approximate per cent invert sugar} = y.$$

$$\text{III. } \frac{100 \text{ Pol.}}{\text{Pol.} + y} = R, \text{ relative number for sucrose.}$$

$$100 - R = I, \text{ relative number for invert sugar.}$$

$$R : Z, \text{ relation of sucrose to invert sugar} = 6.$$

$$\text{IV. } \frac{\text{Cu}}{p} \times F = \text{correct percentage of invert sugar.}$$

In these formulæ Cu is the weighed copper, p the amount of substance taken, pol. the polarisation, Z facilitates reading the vertical column, and $R : Z$ the horizontal column of the following table.

To use the table find the columns agreeing most closely with the values found for Z and $R : Z$. When these columns meet, the value of factor F will be found.

Factors for the Determination of Invert Sugar in the presence of Sucrose.

Sucrose : invert sugar =	M.grms. invert sugar = Z.									
R : Z.	245.	225.	200.	175.	150.	125.	100.	75.	50.	
90 : 10	56.2	55.1	54.1	53.6	53.1	52.6	52.1	51.6	51.2	
91 : 9	56.2	55.1	54.1	53.6	53.1	52.6	52.1	51.6	51.2	50.7
92 : 8	56.2	54.6	53.6	53.1	52.1	51.6	51.2	50.7	50.3	
93 : 7	55.7	54.1	53.6	53.1	52.1	51.2	50.7	50.3	49.8	
94 : 6	55.7	54.1	53.1	52.6	51.6	50.7	50.3	49.8	48.9	
95 : 5	55.7	53.6	52.6	52.1	51.2	50.3	49.4	48.9	48.5	
96 : 4			52.1	51.2	50.7	49.8	48.9	47.7	46.9	
97 : 3			50.7	50.3	49.8	48.9	47.7	46.2	45.1	
98 : 2			49.9	48.9	48.5	47.3	45.8	43.3	40.0	
99 : 1			47.7	47.3	46.5	45.1	43.3	41.2	38.1	

Factors = R.

Example.—The polarisation of a sugar is 86.4 and 3.256 grms. substance = p is equivalent to 0.290 grm. copper = Cu, then :—

$$I. \frac{Cu}{2} = \frac{0.290}{2} = 0.145 = Z.$$

$$II. Z \times \frac{100}{p} = 0.145 \times \frac{100}{3.256} = 4.45 = y.$$

$$III. \frac{100 \times \text{pol.}}{\text{Pol.} + y} = \frac{86.40}{86.4 + 4.45} = 95.1 = R.$$

$$100 - R = 100 - 95.1 = Z; R : Z = 95.1 : 4.9.$$

By consulting the table we find that column 150 comes nearest to $Z = 145$, and column 95.5 is nearest to $R : Z = 92.1 : 4.9$.

Where these columns meet we find the factor 51.2, which enters into the last calculation.

$$IV. \frac{Cu}{p} \times F = \frac{0.290}{3.256} \times 51.2 = 4.56 \text{ per cent invert sugar.}$$

To convert this into saccharose, we subtract $\frac{1}{2}$; $4.56 - 0.23 = 4.33$; add this figure to the direct polarisation and calculate the coefficient of purity from this and the degree Brix.

III.—The Presence of Raffinose must be Considered.

If the chemist is required to consider the presence of raffinose he must proceed as follows :—

(a). The direct polarisation of the sugar is determined, as also (b) the indirect polarisation at exactly 20° C.

The same precautions must be taken in making the inversion as in I. and II. Half the normal weight is dissolved in 75 c.c. of water in a 100 c.c. flask, 5 c.c. hydrochloric acid (38.8 per cent HCl) added, and heated for seven and one-half to ten minutes to 60 to 70° C. After making up to the mark and clarifying with washed bone-black, the reading is taken at exactly 20° C. The following formula serves to calculate the result :—

$$Z (\text{sugar}) = \frac{0.5188 P - J}{0.845}, \text{ and } R (\text{raffinose}) = \frac{P - Z}{1.85};$$

when P = direct polarisation and J = invert reading for normal weight, the prefixed sign having been changed.

The invert sugar is determined as in other syrups. If the test described in Article A shows it to be present in quantities of less than 2 per cent, then it need not be further considered. Two per cent or more of invert sugar must be determined quantitatively according to Meissl's method, described in II., and calculated as saccharose. In finding the factor of this table, raffinose is to be considered as sucrose and Meissl's value. Pol. is therefore the sum of sucrose and raffinose. The coefficient of purity is calculated from the degree Brix and the total sucrose (that is, sucrose + invert sugar calculated to sucrose), the raffinose not being considered.

Example.—The examination of a syrup gave 85.6° Brix, 76.6 direct polarisation, —3 Pol. after inversion. By using the above formula we find 50.5 sucrose and 14 raffinose. There were also found 2.1 per cent sucrose as invert sugar. Therefore the total sucrose is 52.6 and the coefficient 61.4.

Rank deceptions might be practised by adding small amounts of starch sugar syrup to very pure syrups and requesting an examination with regard to raffinose present. In such cases the above method would cause an error in finding too small a sugar content and a considerable amount of raffinose corresponding to the starch sugar added.

The application of this method for the examination of syrups supposed to contain raffinose is hence only possible when no starch sugar is present. If starch sugar is known to be present, then the method described in II. must be used.

The estimation of starch sugar cannot be made exactly as described in II. for syrups in general, as syrups containing raffinose give a different invert reading.

If, therefore, a product is to be examined which is supposed to contain raffinose, it is best to use method No. III., and calculate sucrose and raffinose from this. The observed readings should not vary more than $\pm 5^\circ$ from the calculated readings, otherwise starch sugar is certainly present and the raffinose formula no more applicable. In such a case the syrup must be examined according to II.

(To be continued.)

THE ACTION OF WATER UPON GLASS.

By F. MYLIUS and F. FÖRSTER.

THE authors summarise their rough researches in the following propositions, which they consider proved by their own observations and those of Pfeiffer and Kohlrausch :—

1. The solution of glass in water depends on a decomposition in which, in the first place, free alkali appears.

2. The silica of the glass is secondarily dissolved by the free alkali.

3. The constituents of the solution vary according to the conditions of digestion.

4. The quantity of alkali which passes into solution from a given surface under given conditions is a measure for the attackability of the glass under these conditions.

5. The attackability of surfaces of glass by cold water decreases at first very rapidly with the duration of digestion, and subsequently approach constant values.

6. Different sorts of glass display a different persistence of the solution. (By this term Kohlrausch characterises the relation of its solubility after a prolonged digestion to its original solubility).

7. The attackability of glass increases very rapidly with a rising temperature.

8. The relation of the attackabilities of different kinds of glass depends on temperature.

9. From glasses of equal attackability unequal weights may pass into solution.

10. The attackability of good glass is decidedly decreased by a previous treatment with water.

11. The worse a glass the less its attackability is diminished by treatment with water.

12. The attackability of glass surfaces is modified by "weathering."

13. After treatment with water, surfaces of glass have the property of taking up alkali from the solutions which have been formed, and of giving it up again on renewed treatment with water.

14. Potash glasses are much more soluble than soda-glasses, but the differences disappear in proportion as the glass is richer in lime.

15. In the substance of glass vessels, which are not readily attacked by cold and hot water, the lime, alkalies, and silica must bear a certain proportion to each other.

16. Among the best known glasses plumbiferous flint glass is least soluble in water, but it is corroded at its surface and easily decomposed by acids.—*Zeit. Anal. Chem.*

A REVISION OF THE ATOMIC WEIGHT
OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 58).

It has been said that these experiments were intended only for rough comparison. Since it appeared possible to apply a corresponding correction to the atomic weight of copper deduced from the oxide, it became important to make a more accurate series of determinations. The cupric oxide used in these final experiments represented three different specimens, similar to or identical with those used in Nos. 43, 45, 48, and 49.

Occluded Gas in Cupric Oxide.—Third Series.

Number of ex- periment.	CuO taken. Grms.	Gas evolved. [Apparatus.] C.c.	Temperature of gas. Centi- grade.	Atmospheric pressure. M.m.	Per cent of ni- trogen in CuO by weight.	Per cent of oxy- gen in CuO by weight.
103.	1.84	1.38 (bulbs)	25°	757	0.080	0.003
104.	1.80	1.55 (flask)	22°	763	0.094	0.004
105.	1.30	1.10 (bulbs)	24°	760	0.090	0.004

Average .. . 0.088 0.004

The cupric oxide of the last determination was ignited for three hours in a stream of air, and for twenty minutes in a stream of oxygen, at a medium red heat. It was impossible to determine whether the material had reached constant weight, for the hard glass tube in which the ignition was conducted was very much altered by the heat.

As might have been expected, the very pure cupric oxide employed in these experiments contained a slightly greater amount of occluded gas than the less carefully prepared material of the earlier experiments. Since the latest samples of material were precisely similar to those used in the quantitative analysis of cupric oxide, it is fitting that the latest correction should be applied to those quantitative results. The 2.97909 grms. of cupric oxide used in Experiments 48 and 49 must have contained 0.00276 gm. of occluded gas. That is to say, 2.97633 grms. of pure cupric oxide correspond to 2.37811 grms. of metallic copper. The difference between these weights now really represents the weight of combined oxygen present. The atomic weight of copper upon this basis is easily found to be 63.605.

Correcting the indirect results from the synthesis of cupric sulphate in the same way (see *ante*) the number 63.603 is obtained. Averaging this result with that immediately above, the value 63.604 is found as a mean of five determinations including two wholly distinct methods.

Since it is impossible to learn exactly the amount of gas occluded by Hampe's cupric oxide, the correction of his results will not be attempted. The residue left after the ignition of cupric sulphate can hardly contain any nitrogen; and this supposition more than accounts for the difference between the results of Baubigny's analysis and the present syntheses of cupric sulphate (see p. 21).

Upon referring to the other work upon the atomic weight of copper, it is apparent that nearly all the discrepancies have been explained. A portion of Millon and Commaille's work consisted of weighing the water formed by the reduction of cupric oxide; the reason of the low result of this part of their work is not even now evident, but at the present day a discussion of the possible causes of its error would be unprofitable. Shaw's recent result,

which formerly ranked among the highest of the observed values, now appears among the lowest.

Evidently the occlusion of nitrogen by cupric oxide must have a very serious effect upon experiments in which oxygen is determined by the loss of weight of material prepared by the ignition of the basic nitrate; notably in the determination of the atomic weight of the element after the method of Dumas. When the oxide is obtained by the ignition of the metal in oxygen, the correction is of course inapplicable. Unfortunately, most of the experimenters upon the subject have omitted to state the source of their cupric oxide. The preparation used in the later experiments of Erdmann and Marchand (*Four. für Prakt. Chemie.*, xxvi., 461) must have contained nitrogen; and it will be remembered that the second series of his results gave a much higher result than the first.

In view of the correction, it is remarkable that the resultant atomic weight of oxygen in this case was not even higher than 16; for the correction is about five times as large as the amount necessary to account for the difference between 15.87 and that figure. From a difference either in the mode of preparation or in the temperature of ignition, the oxide used by Erdmann and Marchand must have contained much less nitrogen than the amount found in Experiments 103 to 105; or else some opposite error must have partially counterbalanced this one. Considering the remoteness of all the experiments, a present discussion of the results is unnecessary; but the conclusions are at least sufficient to throw a serious doubt upon the applicability of cupric oxide for a quantitative source of oxygen, as well as to support the modern low atomic weight of that element. The presence of nitrogen could not seriously influence the results of Keiser or those recently obtained here; and it is evident that the material used by Noyes could have contained no occluded gas.

The use of cupric oxide prepared from the nitrate must also introduce a serious error into organic nitrogen determinations after the method of Dumas, as Frankland and Armstrong have already pointed out. The usual "wire form" of cupric oxide is not subject to this cause of inaccuracy, however.

In the near future other oxides will be investigated at this laboratory with regard to their possible occlusion of gases.

(To be continued.)

ANALYSIS OF RUBBER GOODS.

By H. JOSHUA PHILLIPS, F.I.C., F.C.S.,
Analyst to the Great Eastern Railway.

THE following analysis recently made by the writer of an indiarubber mat that has been in constant use at one of the City hotels for over nine years may be of interest to some readers of the CHEMICAL NEWS:—

Moisture .. .	0.50
Silica .. .	1.38
Oxide of iron and alumina .. .	0.70
Zinc oxide .. .	3.51
Sulphur .. .	3.97
Barium sulphate .. .	3.74
Chalk .. .	31.94
Caoutchouc .. .	54.26

100.00

The mat, which was originally 5-8ths of an inch thick, was very little the worse for wear, but had become somewhat brittle. A fracture viewed under a lens showed that the ingredients were not very homogeneously blended. A somewhat new departure in rubber mat-making is the insertion of layers of canvas with the object of preventing cracking, and this appears to answer well for the purpose.

Stratford, London.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

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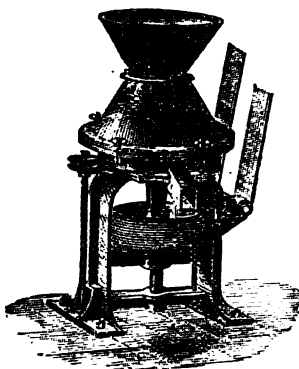
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The STUDENTS' NUMBER of the CHEMICAL NEWS will be published on Friday, September 10th. Gentlemen holding official positions in the Universities, Medical Schools, &c., of the United Kingdom, where Chemistry and Physical Science form a part of the education, who have not yet forwarded the necessary information to our Office for publication in that Number, will confer a favour by sending it with the least possible delay.

Advertisements for this Number should reach the Office not later than Wednesday, the 8th Sept.

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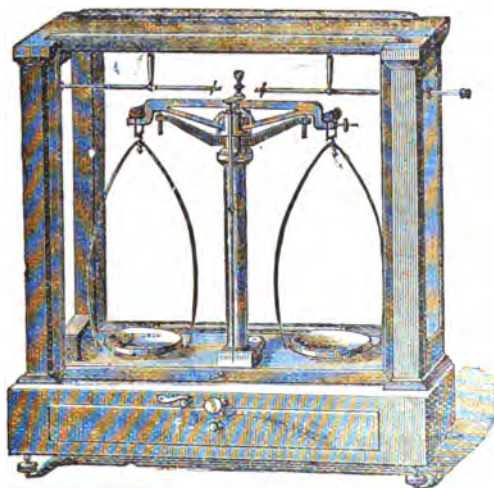


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THE CHEMICAL NEWS.

VOL. LXVI., No. 1707.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

EDINBURGH, 1892.

By Prof. HERBERT McLEOD, F.R.S., F.C.S.,
President of the Section.

IN endeavouring to prepare myself to properly fulfil the duties of President of this Section, to which I have been elected, and for which honour I am much indebted to the council and members of the Association (although I am only too well aware that the position might have been more efficiently filled by many others), I naturally looked at the reports of the previous meetings held in Edinburgh in 1834, 1850, and 1871, and it appears that on the first two occasions an address was not given by the president, a custom the discontinuance of which I have, at the present moment, much reason to regret.

At the meeting in 1834 a committee was appointed consisting of Dr. Dalton, Dr. Hope, Dr. T. Thomson, Mr. Whewell, Dr. Turner, Professor Miller, Dr. Gregory, Dr. Christison, Mr. R. Phillips, Mr. Graham, Professor Johnston, Dr. Faraday, Professor Daniell, Dr. Clark, Professor Cumming, and Dr. Prout, to report at the next meeting their opinion on the adoption of an uniform set of chemical symbols, Dr. Turner to be secretary.

In the following year the report contains: "Report of the Committee on Chemical Notation." Dr. Turner, the chairman of the committee appointed to take into consideration the adoption of an uniform system of chemical notation, made a report to the following effect:—

"1. That the majority of the Committee concur in approving of the employment of that system of notation which is already in general use on the Continent, though there exists among them some difference of opinion on points of detail.

"2. That they think it desirable not to deviate in the manner of notation from algebraic usage except so far as convenience requires.

"3. That they are of opinion that it would save much confusion if every chemist would always state explicitly the exact quantities which he intends to represent by his symbols.

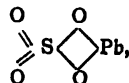
"Dr. Dalton stated to the Chemical Section his reasons for preferring the symbols which he had himself used from the commencement of the atomic theory in 1803 to the Berzelius system of notation subsequently introduced. In his opinion regard must be had to the arrangement and equilibrium of the atoms (especially elastic atoms) in every compound atom, as well as to their number and weights. A system either of arrangements without weights, or of weights without arrangements, he considered only half of what it should be."

We can all sympathise with the members of the section of 1834 in their desire to obtain a uniform system of chemical notation, for at that time several very different systems seem to have been in use. Although the report is a short one, it probably directed the attention of chemists to the desirability of avoiding confusion by the use of various systems, and since that period many advances have been made.

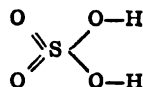
There is now little necessity for every chemist to "state explicitly the exact quantities which he intends to represent by his symbols," for the accurate determinations of atomic weights by many chemists—and we must not omit to mention the work of Stas (whose death we have had to deplore since the last meeting of the British Association)

—have given us a series of numbers which are in the hands of all chemists, so that, except in the cases where great refinement is requisite (or when the atomic weight has not been universally accepted), there is no need to state the values of the symbols.

That great advances have been made in chemical notation is well known to all; even in my own short experience I have had to learn several different methods. When I began to work at chemistry I was told that sulphate of lead was to be expressed by the formula PbO_2SO_3 . Hofmann taught me that it should be PbSO_4 ; then Gerhardt doubled the atomic weights of oxygen and sulphur, and the formula became Pb_2SO_4 ; Cannizzaro showed that the atomic weight of lead should also be doubled, and the formula again became PbSO_4 , but representing twice as much as formerly; then Frankland taught me to write SO_2PbO as the expression of the graphic formula—



which not only states that the compound contains 207 of lead, 32 of sulphur, and 64 of oxygen, but that the sulphur is hexad, and is combined with two atoms of dyad oxygen, and with a dyad compound radical containing one atom of lead and two of oxygen; and of all the formulæ just given this is the only one which satisfies the requirements which Dalton thought necessary in 1835, namely, to indicate not only the weights of the elements present, but also their arrangement. It may be objected that we do not know that this formula really represents the arrangements of the atoms in plumbic sulphate, but there can be very little doubt that the four atoms of oxygen in the compound are not all in the same condition, for if we examine the properties of sulphuric acid (from which the sulphate of lead is derived by the replacement of the hydrogen by lead), we find that two of the atoms of oxygen are more closely associated with the hydrogen than are the other two, and as there is some evidence, although perhaps not very conclusive, that sulphur may be capable of combining with six monad atoms, although no such compound is yet known, it does not seem unreasonable to suppose that sulphuric acid is really—



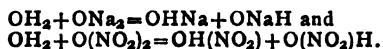
What the nature of the attraction that holds the atoms together may be is not known, but it is more probably of a character similar to that of gravity which holds together sun and planets, than of the nature of cohesion which would hold the atoms rigidly together; the atoms in each molecule are therefore most probably in a state of rotation around, or of vibration to and from, the central atom which holds them together. The pictorial representation in a plane does not therefore truly express the position of the atoms, but merely the relations existing between them. In organic chemistry the use of formulæ expressing such a relation has become indispensable, and in inorganic chemistry I believe such a system is very useful.

Recently this system has been found insufficient for the requirements of organic chemistry, and recourse has been had to the figure of a tetrahedron to represent the atom of carbon, other atoms being attached to the solid angles; in this way the position of the atoms in space is more or less expressed.

There are many cases, however, in which the atomicity theory fails us. At first it seemed probable that the atomicity of an element varied in pairs of attractions, that is, an element might be monad, triad, or pentad, but not dyad or tetrad; or it might be dyad, tetrad, or hexad, but not triad or pentad; but some great difficulties have been

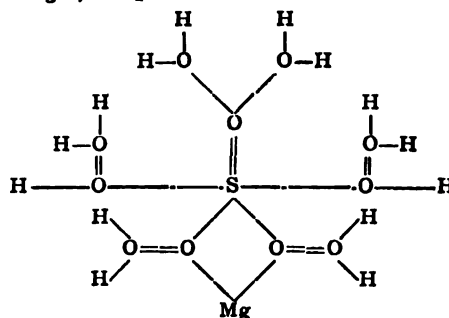
encountered. Thus nitrogen, which is pentad in ammoniac chloride and triad in ammonia, forms the compound nitric oxide, NO, in which it would appear to be dyad; it has been suggested, however, that in this body the nitrogen is really triad, and that it possesses a "free bond." Now the idea of a "free bond" seems contrary to the principles of atomicity, since it is on the belief that such a free bond is impossible that the explanation of the existence of elementary molecules is found, for it is said that when hydrogen is liberated two atoms unite to form a molecule, so that their mutual attractions may be satisfied. Nevertheless, nitric oxide is a very active body, uniting readily with other substances, so the free bond seems to be on the look out for other kinds of matter, but to have no attraction for the free bond of another molecule of nitric oxide. As the molecule of nitric peroxide is variable by alterations of temperature, being N_2O_4 at low and NO_2 at high temperatures, it seemed not impossible that at the ordinary atmospheric temperature nitric oxide was a simplified or dissociated molecule, and that if the temperature were sufficiently reduced it would be found that its molecule would be N_2O_2 , and thus it would contain triad nitrogen without a free bond. The density of the gas has, however, been determined at a temperature as low as -73° , and the molecule is still NO. Another important exception to the variation of the atomicity of an element in pairs was furnished by the investigations of Sir Henry Roscoe on the chlorides of vanadium; this element, which, from analogy, should be a triad or a pentad, appears to form a chloride of the composition VCl_4 . Again, the molecule of peroxide of chlorine is ClO_2 , which would make chlorine a tetrad or the compound must have a free bond.

Another set of phenomena which the atomicity theory will not explain is the existence of well-defined crystalline salts containing what is called water of crystallisation. This water is in many cases held with considerable pertinacity, the body appearing to be a veritable chemical compound. But water appears to be a saturated body, the attractions of the oxygen being satisfied by those of the hydrogen. It is true that water acts vigorously on other compounds, as on metallic oxides to form hydrates, and on some anhydrides to form acids, but these appear to be phenomena of double decomposition; thus the combination of water with sodic oxide and nitric anhydride respectively may be expressed by the equations—

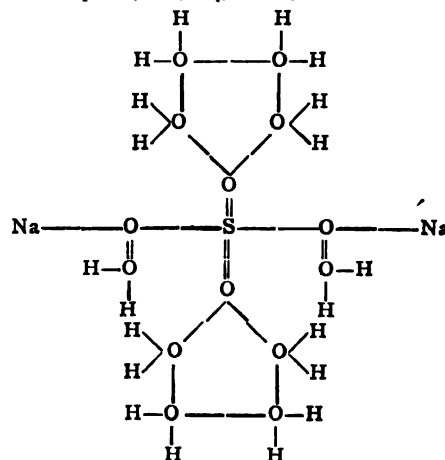


In the combination of water with an anhydrous salt, a phenomenon often accompanied by great rise of temperature, there does not appear to be a double decomposition. That there is a chemical combination of some sort is shown by the changes of properties produced, crystalline form and colour being both sometimes altered. Compounds so produced have been called "molecular compounds" to imply that saturated molecules are in some way or another combined, the combination being different from "atomic combination," in which the atoms are directly united according to their valencies. Another explanation has been suggested by assuming that there is some "residual affinity" not saturated by the constituents of the body, and that this residual affinity enables bodies to unite in a less stable manner than in most compounds. But are not these terms—"molecular combination" and "residual affinity"—analogous to the term "catalysis," merely words to express—not to explain—what we do not understand? If "residual affinity" really exists, it must reside in the oxygen of the water, or in the hydrogen, or in both; if so, what will happen to some of the complex constitutional formulæ of the organic chemist in which the carbon is tetrad, the oxygen dyad, and the hydrogen monad? If any of these elements have a residual affinity should we not expect to find additional unions between some of the atoms of the same molecule over and above those represented by the formula?

Oxygen may be tetrad, for which there is evidence in OAg_4 . Under these circumstances water is by no means a saturated compound, and there would be no difficulty in explaining the combination of water with oxygen salts. Thus crystallised magnesian sulphate, $MgSO_4 \cdot 7OH_2$, or SOH_2MgO , $6OH_2$ would be—



and sodic sulphate, $Na_2SO_4 \cdot 10OH_2$:—



Even alum, with its 24 molecules of water of crystallisation, may be expressed by an appalling formula :—(See next page).

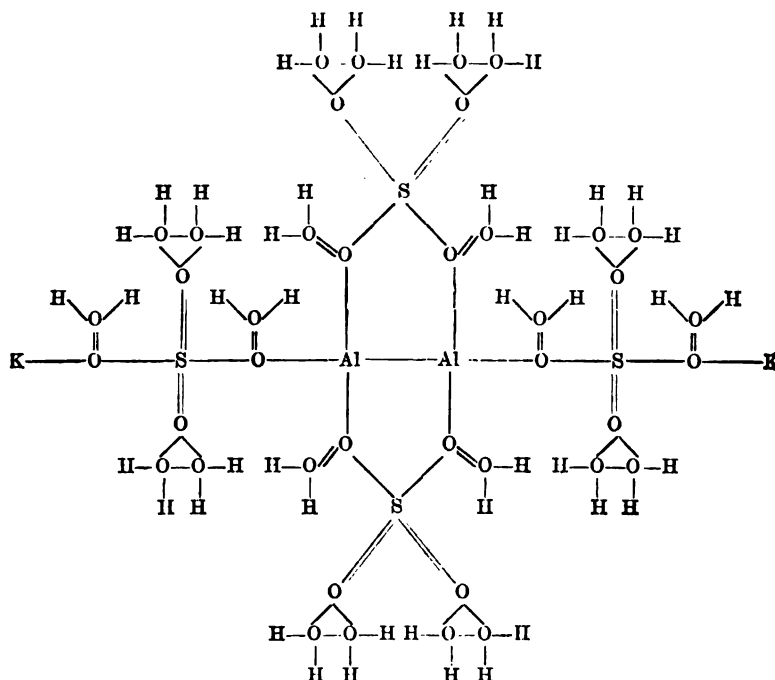
There is certainly a symmetry about the formula, and it will be found that 16 of the molecules of water are in a different position from the remaining 8; this probably has no significance, although Graham found that crystallised alum at a temperature of 61° lost 18 molecules of water; if he had used a temperature a few degrees lower he might have found that only 16 passed off!

By a little stretching of the imagination and altering the atomicities of the elements to suit each particular case, no doubt graphic formulæ might be made for all crystalline salts, but they would be perfectly artificial, and not much good is likely to come from the attempt.

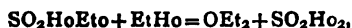
I fear we are driven to the conclusion that, notwithstanding all the progress that has been made in chemical science during the last fifty-eight years, we have not yet reached a method of notation that would have satisfied Dr. Dalton in 1834.

But since that time we have learnt that our formulæ ought to show even more than the number and position of the atoms of a compound; we should like them to indicate the amount of potential energy residing in a body, and our equations ought to indicate the amount of heat generated by a chemical change. Let us hope that before the next meeting of the British Association in Edinburgh these desirable developments will have been accomplished.

A short time ago I mentioned the word catalysis as



being employed to express certain chemical actions which cannot be explained. It is applied to those phenomena which take place in the presence of a body which appears to be entirely unchanged by the action. Happily these catalytic actions are being explained one after another, so that soon the name itself may become obsolete. An example of this action of presence may be given. When a mixture of sulphuric acid and alcohol is heated to a temperature of about 140° to 150° , ether passes over. Now alcohol contains C_2H_6O , and if from two molecules of alcohol one molecule of water is subtracted, a molecule of ether results: $2C_2H_6O = OH_2 + C_4H_{10}O$. As sulphuric acid is known to have a great attraction for water, it is easy to imagine that the acid combines with the water and ether passes off. But it is found that a small quantity of sulphuric acid at the temperature of 140° to 150° will transform a very large amount of alcohol into ether and water, much more than can be explained by assuming that the acid has combined with the water. If a mixture of sulphuric acid and alcohol is heated to a temperature of 140° to 150° , and alcohol allowed to flow into the liquid, a mixture of ether and water vapours passes over, and after a large quantity of alcohol has been transformed, the amount of sulphuric acid is found to be unaltered. At first glance this seems very difficult to explain, but on further investigation it is found that alcohol and sulphuric acid act one on another to form ethyl-sulphuric or sulphovinic acid: $SO_2HoEt + EtHo = SO_2HoEtO + OH_2$; but when ethyl-sulphuric acid is heated with alcohol, ether is formed with the reproduction of sulphuric acid—



the sulphuric acid is then able to produce ethyl-sulphuric acid by acting on more alcohol, so a continuous production of ether and water takes place without loss of sulphuric acid. Another well-known action is the combination of oxygen and hydrogen under the influence of spongy platinum. In this case the platinum remains apparently unaltered, and is capable of causing the combination of any quantity of mixed gases. As spongy platinum possesses the power of absorbing large quantities of gases, it is usually said that the molecules of

oxygen and hydrogen are so much condensed in the platinum that they are brought within the sphere of one another's attractions, and consequently combine.

Another instance of an action of this kind is afforded by the oxidation of ammonia in the presence of chromic oxide. When ammonic dichromate is heated an evolution of gas occurs, and a residue of chromic oxide is left which bears a striking resemblance to a mixture of black and green tea; when some of this substance is placed on a piece of wire gauze, heated, and then supported over a vessel containing a strong solution of ammonia, the oxide glows in a manner similar to the glowing of spongy platinum under the influence of a mixture of hydrogen and air. Under these conditions the chromic oxide facilitates the oxidation of the ammonia, but it becomes changed during the process; instead of having the appearance above described it acquires a bright green colour. Now, we know that chromium is capable of forming several combinations with oxygen. Is it therefore too much to suppose that the chromium is alternately oxidised by the oxygen of the air, and reduced by the hydrogen of the ammonia, so that although in the end it has the same composition as at the beginning, nevertheless it has been continuously decomposed and reproduced? Now, may not a similar change take place during the action of spongy platinum on a mixture of hydrogen and oxygen? The alteration of the platinum is very slight, but I believe I have observed a slight modification of the appearance of a fragment of spongy platinum, that was kept glowing by a small jet of purified hydrogen for some hours, the gas not being allowed to burn so as to heat the platinum to a very high temperature, the metal appears to be compacted and to be covered by minute spherules of glistening metal. Now, may not the platinum have entered into combination with one or other of the gases, and been subsequently reduced? If this is the true explanation, then we have in this case a continuous series of chemical changes and the "catalysis" is explained.

We all know the ease with which oxygen is obtained from potassic chlorate when heated with a small quantity of oxide of manganese; the quantity of peroxide is the

same at the end of the process as at the beginning, and it may be used over and over again to assist in the decomposition of fresh potassic chlorate. The oxide of manganese undergoes a molecular alteration; if a crystalline variety is employed, it is found at the end of the process to have been transformed into fine powder.

I hope I have proved to the satisfaction of my brother chemists that potassic permanganate is first formed and subsequently decomposed with the reproduction of manganese peroxide.

Oxide of cobalt possesses the remarkable property of decomposing solutions of hypochlorites at moderate temperatures with evolution of oxygen. For some time I have been endeavouring to find the explanation of the change, but hitherto without complete success. At first it seemed probable that an unstable cobaltate, analogous to a ferrate, was formed and decomposed at the temperature of the experiment. In fact, oxygen is evolved when chlorine is passed through a boiling solution of sodic hydrate containing ferric hydrate in suspension. But no evidence of the existence of a cobaltate could be found. When a cobaltous salt is added to an alkaline solution of a hypochlorite, a black precipitate is formed which is usually stated to be cobaltic hydrate, $\text{Co}_2\text{H}_2\text{O}_6$, but Vortmann has shown that when a cobaltous salt is mixed with a solution of iodine in potassic iodide, and the liquid rendered alkaline by sodic hydrate, the precipitate formed at a temperature between 50° and 60° approaches in composition the dioxide of cobalt, CoO_2 . He also found that the precipitate lost oxygen at the temperature of boiling water. I have repeated some of his experiments, and can quite confirm them, although I have not obtained an oxide containing quite as much oxygen as his richest oxide. The oxides I prepared rapidly effected the decomposition of a solution of sodic hypochlorite, and that without undergoing any loss of oxygen themselves; in fact, in the two experiments made, the cobalt compound contained a little more oxygen after boiling with the hypochlorite.

We have now many instances of the influence which small quantities of substances have upon chemical reactions. These influences may be more common than is generally supposed. The presence of a third body is frequently helpful in the combination of elements with one another: thus dry chlorine will not attack melted sodium or finely divided copper; an electric spark will not cause a dry mixture of carbonic oxide and oxygen to explode; carbon, phosphorus, and sulphur will not unite with dry oxygen, and as chemical science progresses we may find that many well-known actions are conditioned by the presence of minute traces of other matter which have hitherto escaped detection. We all know the profound alterations of the properties of substances by minute traces of impurities; less than one-tenth per cent of phosphorus will render steel unfit for certain purposes. The sapphire and ruby only differ from colourless alumina by the presence of traces of impurities hardly recognisable by chemical analysis. During this meeting we hope to have a contribution to the section on the influence of minute traces of what may be called impurities on the properties of different substances and their influence on chemical changes.

In this city, where the first public chemical laboratory was started in 1823 by Dr. Anderson, the assistant of Prof. Hope, it is hardly necessary to insist on the extreme importance of teaching chemistry by practical work, but unfortunately, even at the present time, endeavours are made to teach the subject by means of lectures (sometimes without experiments) or by reading. Those who are acquainted with chemistry well know the impossibility (this is hardly too strong a word) of learning the science, especially in the first stages, without actual experiment, by which a practical acquaintance with chemical phenomena is obtained. The attempt to learn chemistry without practical experience reminds one of the well-known story (for the truth of which I will not vouch) of a mathe-

matician who lectured on natural philosophy; he was visiting a foreign laboratory, and stopped before a piece of apparatus and asked what it was: on being told it was an air-pump he exclaimed: "Dear me! I have lectured on the air-pump for twenty-five years, and this is the first time I have seen one." It is problematical if his students can have derived much advantage from his lectures. Teaching of the kind to which reference has just been made is generally given to candidates for examinations who do not intend to take up chemistry as their chief subject. At the present time chemistry is required for entrance and preliminary examinations from many classes of students. There is no doubt that it is an excellent means of education, teaching a boy to observe and draw conclusions from his observations; but if he makes no observations it is little more than useless cram, the memory might as well be exercised by learning a novel by heart.

This imperfect mode of teaching chemistry arises principally from the difficulty of obtaining properly appointed laboratories in schools, in addition to which the very strong fumes are sometimes disagreeable, making it inconvenient to have them in or near a house, to say nothing of the possible dangers to the clothes and their contents; but there is no help for it, the teaching must be accompanied by experimental demonstration, as was indicated in the Reports on the teaching of chemistry which have been presented to this Association in former years. It must be admitted that examinations do not always discover the best student; many are capable of preparing for examinations with a small knowledge of their subject, others, with a good knowledge, fail from nervousness or other causes, but at the present time, examination, although far from perfect, is almost the only means we have of judging the fitness of the candidate. By properly selecting questions the examiner may, to a considerable extent, discourage cram; he should endeavour to find out what the pupils have actually seen, and to make them draw conclusions from facts which they have either themselves observed, or which have been described to them; it is only in this manner that chemistry can be used as a means of mental training.

These remarks do not apply to the education of students intending to make chemistry their profession, who have many opportunities in the large laboratories of Great Britain and the Continent of obtaining all the necessary instruction. The Institute of Chemistry, which was founded to improve the status and also the education of professional chemists, requires that its members should have a thoroughly scientific training. Before a candidate for the associateship is admitted to examination, he must bring evidence that he has passed satisfactorily through a systematic course of at least three years' study in the subjects of theoretical and practical chemistry, physics, and elementary mathematics, in some recognised college or school; and before admission to the fellowship he must have passed through three additional years of work in chemistry. It is to be hoped that an example of this kind will ultimately have a good effect in improving the modes of teaching the science in its elementary stages.

There is another class of workers in chemistry who must not be forgotten at the present time, as they have much influence on the life of the world, and have been working for ages, but have only recently been recognised. I mean those organisms which are included under the name of microbes. These organisms are capable of producing chemical changes which entirely surpass all the results hitherto obtained by the chemist in his laboratory. That the transformation of sugar into alcohol and carbonic anhydride in the ordinary process of fermentation is due to a living organism, has been known for some years; the important transformation of ammonia into nitrous and nitric acids in the soil has been shown to be due to organisms which have recently been investigated by many chemists; it is possible to transform ammonia into these acids in the laboratory by oxidation

under certain conditions and at a high temperature, whereas the organism does the work quite as efficaciously at the common temperature. Other organisms have the power of producing complex organic poisons by the alteration of some of the constituents of the animal body, and the relation of these products to the study of diseases is of the highest possible importance. As we hope to have a discussion on this interesting subject by many eminent authorities, both from the chemical and biological points of view, it will be unnecessary to pursue the subject further, unless it be to urge some of the younger chemists to work at the chemical aspect of bacteriology. They must be prepared for hard work and many disappointments, for the subject is undoubtedly a difficult one.

I cannot conclude this address without reference to the great loss which chemistry has sustained by the death of Prof. A. W. von Hofmann. I had the good fortune to be under him as student and assistant from 1856 until he left this country in 1865; all who worked with him must have been deeply impressed by his capacity for work and his power of inducing work in others. Although perhaps some of us did not appreciate this at the time, yet we feel we owe him a debt of gratitude for his having started us in the right way. The list of papers under his name in the Royal Society Catalogue up to the year 1883 is 299, written by himself alone, besides twenty-two joint papers. One of his characteristics which impressed me was his investigation for the purpose of furthering chemical knowledge without any view to practical applications, and I well remember his lecture at the Royal Institution, in 1862, on Mauve and Magenta (which owed so much of their success to his work), in which he produced the original specimen of benzene which had been obtained by Faraday from oil-gas in 1825. He pointed out that Faraday had prepared this substance and investigated its properties without ever supposing that it could have any practical application. The following is the concluding paragraph of the lecture:—

"Need I say any more? The moral of Mauve and Magenta is transparent enough; I read it in your eyes. We understand each other. Whenever in future one of your chemical friends, full of enthusiasm, exhibits and explains to you his newly-discovered compounds, you will not cool his noble ardour by asking him that most terrible of all questions, 'What is its use? Will your compound bleach or dye? Will it shave? May it be used as a substitute for leather?' Let him quietly go on with his work. The dye, the lather, the leather will make their appearance in due time. Let him, I repeat it, perform his task. Let him indulge in the pursuit of truth—of truth pure and simple—of truth not for the sake of Mauve, not for the sake of Magenta, let him pursue truth for the sake of truth."

This seems to me the true spirit of the scientific investigator, and in many cases the reward consists solely in the consciousness that the investigator has done his duty; in some cases the reward may take a more substantial form, and since the above paragraphs were written I have been informed that Professor von Hofmann has left a large fortune, the result of the applications of his discoveries in technical chemistry.

"Vivat Ars Chemica!"—The *Chemiker Zeitung* briefly notices a humorous work under this title from the pen of Dr. C. Geissler. We extract two distichs which we unfortunately cannot render in verse, and which show that even in the Vaterland the position of the chemical profession is not without its shadow-side: "My uncle, the chemist, has reached the age of forty, and last month he received his first salary." "My friend has already reached a tolerable position; no payment, heavy security, but free breathing." In a different direction is the advice: "If a girl pleases you, first test her mother with blue litmus-paper!" The work is published by Fesefeld, of Freiberg, in Breisgau.

ADDRESS
TO THE
MATHEMATICAL AND PHYSICAL SECTION
OF THE
BRITISH ASSOCIATION,
EDINBURGH, 1892.

By Prof. ARTHUR SCHUSTER, Ph.D., F.R.S., F.R.A.S.,
President of the Section.

In opening the proceedings of our Annual Meeting the temptation is great to look back on the year which has passed, and to select for special consideration such work published during its course as may seem to be of the greatest importance. I fear, however, that a year is too short a time to allow us to form a fair estimate of the value of a scientific investigation. The mushroom, which shoots up quickly, only to disappear again, impresses us more than the slow-growing seedling which will live to be a tree, and it is difficult to recognise the scientific fungus in its early stage. But, although I do not feel competent to give you a review of the progress made in our subject during the last twelve months, there is one event to which some allusion should be made. It has been the sad duty of many of my predecessors to announce the death of successful workers in the field of science, but I believe I am unique in having the pleasure of recording the birth of a scientific man. At the beginning of this year there came into the world a being so brilliant that he could, without preparation, take up the work of the most eminent man amongst us. Believers in the transmigration of souls have speculated on the fact that Galileo's death and Newton's birth fell within a year of each other; but no event has ever happened so striking as that which took place on the 1st of January, when the mantle of Sir William Thomson fell on the infant Lord Kelvin. Those who have attended these meetings will feel with me that the honour done to our foremost representative,—an honour which has been a source of pride and satisfaction to every student of science,—could not altogether remain unnoticed in the section which owes him so much.

We are chiefly concerned here with the increase of scientific knowledge, and we derive pleasure in contrasting the minor state of ignorance of our own time with that which prevailed a hundred years ago. But when we contrast at the same time the refined opportunities of a modern research laboratory with the crude conditions under which the experimentalist had to work at the beginning of the century, we may fairly ask ourselves whether it is possible by means of any systematic course of study, or by means of any organisation, to accelerate our progress into the dark continent of science. A number of serious considerations arise in connection with this subject, and though I am not going to weary you by attempting an exhaustive discussion, I should like to draw your attention to a few matters which seem to me to be well worthy of the consideration of this Association. Changes are constantly made and proposed in our existing institutions, or new ones are suggested which are to serve the purpose of a more rapid accumulation of knowledge. I need only allude to the alterations in the curriculum of the science school in our old Universities, made partly for the purpose of fitting their graduates for the conduct of original research, or to the national laboratory proposed by my predecessor in this chair for carrying out a certain kind of scientific investigation, which at present is left undone, or is done by private enterprise. Even our own Association has not escaped the evil eye of the reformer, and, like other institutions, it may be capable of improvement. But in choosing the direction in which a change may best be made, I think we may learn something from the way in which Nature improves its organisms. We are taught by biologists that natural selection acts by developing those qualities which enable

each species best to survive the struggle for existence; useless organs die off or become rudimentary. Nature teaches us, therefore, how a beautiful complex of beings, mutually dependent upon each other, is formed by improving those parts which are best and most useful, and letting the rest take care of itself. But in many of the changes which have been made or are proposed, the process of reform is very different. The weakest points are selected, our attention is drawn to some failure or something in which we are excelled by other nations, and attempts are made to cure what perhaps had better be left to become rudimentary. The proceeding is not objectionable as long as the nourishment which is applied to develop the weaker organs is not taken from those parts which we should specially take care to preserve. To apply these reflections to the question with which we are specially concerned, I should like to see it more generally recognised that although there is no struggle for existence between different nations, yet each nation, owing to a number of circumstances, possesses its own peculiarities, which render it better fitted than its neighbours to do some particular part of the work on which the progress of science depends. No country, for instance, has rivalled France in the domain of accurate measurement, with which the names of Regnault and Amagat are associated, and the International Bureau of Weights and Measures has its fitting home in Paris.* The best work of the German Universities seems to me to consist in the following up of some theory to its logical conclusions and submitting it to the test of experiment. I doubt whether the efforts to transplant the research work of German Universities into this country will prove successful. Does it not seem well to let each country take that share of work for which the natural growth of its character and its educational establishment best adapt it? Is it wise to remedy some weak point, to fill up undoubted gaps, if the soil that fills the gaps has to be taken from the hills and elevations which rise above the surrounding level?

As far as the work of this section is concerned, the strongest domain of this country has been that of mathematical physics. But it is not to this that I wish specially to refer. Look at the work done in Great Britain during the last two centuries; the work not only in physics, but in astronomy, chemistry, biology. Is it not true that the one distinctive feature which separates this from all other countries in the world is the prominent part played by the scientific amateur, and is it not also true that our modern system of education tends to destroy the amateur?

By amateur I do not necessarily mean a man who has other occupations and only takes up science in his leisure hours, but rather one who has had no academical training, at any rate in that branch of knowledge which he finally selects for study. He has probably been brought up for some profession unconnected with science, and only begins his study when his mind is sufficiently developed to form an entirely unbiased opinion. We may, perhaps, best define an amateur as one who learns his science as he wants it and when he wants it. I should call Faraday an amateur. He would have been impossible in another country; perhaps he would be impossible in the days of the Science and Art Department. Other names will occur to you, the most typical and eminent being that of Joule. It is not my purpose to discuss why distinguished amateurs have been so numerous in this country, but I am anxious to point out that we are in danger of losing one great and necessary factor in the origination of scientific ideas.

One of the distinctive features of an amateur is this,

* Much of the good work done by this Bureau remains unknown, owing to the miserly way in which their publications are circulated. No copies are supplied even to the University libraries. The explanation, of course, is "want of funds." In other words, England, France, and Germany, together with other nations, unite to do a certain kind of work, but cannot afford to distribute a few copies of the publication to the public for whose benefit the work is undertaken.

that he carries not the weight of theories, often not the weight of knowledge, and, if I am right, there is a distinct advantage in having one section of scientific men beginning their work untrammelled by preconceived notions, which a systematic training in science is bound to instil. Whatever is taught in early age must necessarily be taught in a more or less dogmatic manner, and in whatever way it is taught, experience shows that it is nearly always received in a dogmatic spirit. It seems important, therefore, to confine the early training to those subjects in which preconceived notions are considered an advantage. It is to me an uncongenial task to sound a note of warning to our old Universities, for the chief difficulties in which they are placed at present are due to the fact that they have given way too much to outside advice; but I cannot help expressing a strong conviction that their highly specialised entrance examinations are a curse to all sound school education, and will prove a still more fatal curse to what concerns us most nearly, the progress of scientific knowledge. If school examinations could be more general, if scientific theories could only be taught at an age when a man is able to form an independent judgment, there might be some hope of retaining that originality of ideas which has been a distinctive feature of this country, and enabled our amateurs to hold a prominent position in the history of science. At present a knowledge of scientific theories seems to me to kill all knowledge of scientific facts.

It is by no means true that a complete knowledge of everything that has a bearing on a particular subject is always necessary to success in an original investigation. In many cases such knowledge is essential, in others it is a hindrance. Different types of men incline to different types of research, and it is well to preserve the dual struggle. The engine which works out the great problems of nature may be likened to a thermodynamic machine. The amateur supplies the steam and the Universities supply the cold water; the former, boiling over often with ill-considered and fanciful ideas, does not like the icy douche, and the professional scientist does not like the latent heat of the condensing steam, but nevertheless the hotter the steam and the colder the water the better works the machine. Sometimes it happens that boiler and cooler are both contained in the same brain, and each country can boast of a few such in a century, but most of us have to remain satisfied with forming only an incomplete part of the engine of research.

But while it is necessary to recognise the great work done by the unprofessional scientists, it seems not untimely to draw their attention to the damage done to themselves if they overstep their legitimate boundaries, and especially if they seek popular support for their theories, which have not received the approval of those who are competent to judge. An appeal from Alexander sober to Alexander drunk will not prove successful in the end.

The gradual disappearance of the amateur may be a necessary consequence of our increased educational facilities, and we must enquire whether any marked advantages are offered to us in exchange. There is one direction in which it would seem at first sight, at any rate, that a proper course of study could do much to facilitate the progress of research.

On another occasion I pointed out that two parties are necessary for every advance in science, the one that makes it and the one that believes in it. If the discoverer is born, and cannot be made, would it not be possible at any rate to train the judgment of our students so that they may form a sound opinion on the new theories and ideas which are presented to them? It is too early as yet to judge in how far our generation is better in this respect than the one that has gone before them, but on closer examination it does not seem to me to be obvious that any marked improvement is possible. Every new idea revolutionising our opinions on some important question must necessarily take time before it takes a proper hold on the

scientific world. Is it not true that any one who can at once see the full importance of a new theory, and accept it in place of the one in which he has been brought up, must stand at a height almost equal to that of the originator? The more startling and fresh the new conception, the fewer must be those who are ready to adopt it. But looking back at the history of science during the present century, is there much evidence that great discoveries have been seriously delayed by want of proper appreciation? We may hear of cases where important papers have been rejected by scientific societies, and occasionally a man of novel ideas may have been too much neglected by his contemporaries. I doubt whether such cases of apparent injustice can ever be avoided, and, simply looking back on the great changes involved in matters of primary importance, such as the undulatory theory of light, the conservation of energy, and the second law of thermodynamics, I cannot admit that there is much reason to be dissatisfied with the rate at which new theories have been received. Those who experience a temporary check, owing to the fact that public opinion is not ripe for their ideas, are often amply rewarded after a lapse of a few years. The disappointment which Joule may have felt during the time his views met with adverse criticisms from the official world of science was no doubt amply compensated by the pleasure with which he watched the subsequent progress of research in the new domain which his discoveries have opened out.

The point is not one of academic interest only, for the fear of repressing some important new discovery has a detrimental influence in another direction. The judgment of the scientific world seems to me to be tending too much towards leniency to apparently absurd theories, because there is a remote chance that they may contain some germ of real value. A new truth will not be found to suffer ultimately by adverse and even unreasonable criticism, while bad theories and bad reasoning, supported by the benevolent neutrality of those to whose judgment the scientific world looks for guidance, are harmful in many ways. They block the way to an independent advance and encourage hasty and ill-considered generalisations. The conclusions I should draw from the considerations I have placed before you are these: I believe that a reasonable censorship exercised by our scientific societies is good and necessary; that those whose fate it is to be called on to express an opinion on some work or theory should do so fearlessly according to their best judgment. Their opinion may be warped by prejudice, but I think it is better that they should incur the risk of being ultimately found to be wrong than that they should help in the propagation of bad reasoning. There is one matter, however, on which all opinions must agree. Worse than bad theory or logic is bad experimental work. Should we then not rigorously preserve any influence or incentive which encourages the beginner to avoid carelessness and to consider neither time nor trouble to secure accuracy? There is no doubt to my mind that the prospect of admission to the Royal Society has been most beneficial in this respect, and that the honourable ambition to see his paper published in the *Transactions* of that Society has preserved many a student from the premature publication of unfinished work.

(To be continued.)

The Dangers of Bacteriology.—According to a medical contemporary a London physician much devoted to the experimental study of microbia met with a shocking end. It was his custom, it appears, to carry in a bag cultures of pathogenic micro-organisms along with his lunch. Some bacillus or allied microbe found its way from the "culture" into the esculents, and the experimentalist paid for his indiscretion with his life. Without more discretion is exercised we shall have the enemies of Science agitating for legislative restrictions on bacteriological research.

METHODS OF SUGAR ANALYSIS.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

(Continued from p. 73).

IV.—Examination of Sugars for Raffinose.

THE method of examining syrups containing raffinose can be applied to sugars. The direct polarisation is taken in the usual manner, the indirect after inversion of one-half the normal weight just as directed for syrups under III. (b), and the content of sucrose and raffinose calculated by means of the formula given in III. Numerous experiments have shown this method to give reliable results. Thus there were found in mixtures of sucrose and raffinose:—

Mixture.		Found by the method.	
Sucrose. Per cent.	Raffinose. Per cent.	Sucrose. Per cent.	Raffinose. Per cent.
97'00	3'00	97'02	2'98
91'00	9'00	90'99	8'95
85'00	15'00	85'06	14'97

Though without doubt this method is very accurate, still a wide limit must be given for experimental errors on account of its novelty. A variation of 0'6 between the sucrose as calculated by the raffinose formula and that determined directly by polarisation has therefore been made the limit. Supposing, for instance, that the sucrose found by direct polarisation is 92'6 and that calculated by the formula 92 per cent, then we may suppose this difference to be caused by errors in the method. In such a case raffinose should be reported absent, and the direct polarisation used for the sugar content. If, however, only 91'9 per cent sucrose were found by the formula while the direct polarisation was 92'6, then the presence of raffinose can not be doubted. To avoid mistakes which may be caused by larger errors than 0'6 it is advisable to make a control determination in all cases where the difference is less than 1 per cent, and to base the presence or absence of raffinose upon the result of this control.

The above limit for errors will not influence the utility of the method, as the percentage of raffinose so far observed in high sugars always corresponded to more than 0'6 per cent of sucrose. No method has yet been proposed for the determination of smaller amounts of raffinose, and they may therefore be neglected. Scheibler's method of calculating small amounts of raffinose by supposing the organic substances not sugar to be equal to the ash is not accurate, as the excess of organic substance over ash is not known.

The method is, however, of value in cases where the result found by the formula varies comparatively little from the polarisation; for instance, corresponding to less than 1 per cent of sucrose. Here it will decide whether raffinose is present or whether the difference is caused by errors.

For this purpose the polarisation, moisture, and ash are determined, the organic substances not sugar taken as equal to the ash, and these four constituents added together. In all cases where raffinose is present the result will be over 100; if it falls below 100, raffinose may be considered absent. In the former case, the percentage of raffinose is calculated as follows:—

The percentage of water plus twice the ash is deducted from 100.

The result corresponds to the percentage of sucrose plus anhydrous raffinose. If we substitute a for the figure thus found, p for the direct polarisation, x for the sucrose present, and y for the raffinose present, then—

$$x + 1'85 y = p$$

$$x + y = a$$

$$x \text{ (per cent sucrose)} = \frac{1'85 a - p}{0'85}$$

$$y \text{ (per cent raffinose)} = \frac{a - 1'85 a - p}{0'85}$$

The limit for error must here be placed at 0.3; that is, the sum of polarisation, twice the ash and moisture must be more than 100.3, if the method is employed. Otherwise the result would be too uncertain for practice, as errors of 0.2 may easily occur in the direct reading. The following example has been so constructed as to show that the method with the above limit of error is not capable of determining variations of 0.6 per cent.

A sugar gave 99.7 polarisation, 0.4 water, and 0.1 ash; then the sum total was—

$$\begin{array}{rcl} & 99.7 & a = 100.0 \\ & + 0.4 & - 0.4 \\ + 2 \times 0.1 & = 0.2 & - 0.2 \\ \hline & 100.3 & a = 99.4 \quad p = 99.7 \end{array}$$

Therefore x (sucrose) = 99.05, which is taken as 99.1, and y (raffinose) = 0.3. It is apparent that the 0.3 plus polarisation, found by this method, and which must be taken as the limit of error, correspond exactly to the variation between actual sucrose and direct reading, which has been made the limit for the inversion method with raffinose formula. The control is unnecessary when a difference of 1 per cent or more is found between the actual sucrose and direct reading. Very often the result of the raffinose formula is taken even if the control gives a negative result. If Scheibler's method gives negative results with a sugar varying less than 1 per cent, then raffinose should be reported absent. If, however, the control leaves any doubt, as when the sum varies between 100 and 100.3, or if raffinose is actually found, then the results obtained by the inversion method should always be reported, as long as the difference between the sucrose found and the direct reading amounts to more than 0.6 per cent. If it is less than 0.6 or just 0.6, then the analyst should report that he is unable to detect raffinose. In calculating the final results hundredths should be taken as an additional tenth; thus 97.01 per cent sucrose is 97.1.

(To be continued).

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Concluded from p. 74).

IV. UPON TYPICAL COPPER.

It has been noticed that most of the calculations described in the present paper have been referred to electrolytic copper. Whether such copper represents the typical element or not is a most important question, but is one which unfortunately cannot be conclusively answered here.

Many authorities have discussed the subject,† and both sulphur and occluded gases have been found in metal prepared in this way. Hampe has shown that the occasional presence of sulphur is probably due to minute drops of solution imprisoned between the electrode and the deposit. When pure copper was to be prepared in the present investigation, the metal was invariably detached from the dish in order to prevent such imprisonment. In the determination of copper already in solution the current was always made as weak as possible in order to avoid the chance of error. Besides, it will be remembered that there was a slight loss rather than a gain during electrolysis.

The occlusion of gases is at worst very slight. In order to reduce the error from this cause to a minimum, the crucible which formed the negative electrode was usually

coated beforehand with copper, that the initial and the final surface might be subject to the same error. To determine the amount of volatile material absorbed by electrolytic copper, very thin strips were ignited in a stream of hydrogen, with the following results:—

	Grm. lost.	Grm.
107	0.80565	0.00005
108	0.67724	0.00004
109	1.24158	0.00004
110	0.80712	0.00001
111	1.00616	0.00003

Average 1 grm. lost 0.00003

This correction is too small to be applied, even supposing that the method of precipitation just mentioned did not render the application unnecessary. The amount of hydrogen absorbed even by copper reduced from the oxide is exceedingly small. Erdmann and Marchand found that one grm. of copper absorbed three one-hundredths of a m.grm. of hydrogen, and Dumas's results were essentially the same.* Hampe was unable to find a trace of the gas in the copper remaining from his experiments. While this correction may have a sensible effect upon the old atomic weight of oxygen, it cannot seriously affect the atomic weight of copper.

No method for the preparation of pure copper has been suggested which is not open to possible objections. The present standard of reference has the merit of simplicity. Moreover, the results of the analysis of cupric sulphate, unless concealing some unknown error, show that electrolytic copper cannot be very different from the typical element as it exists in combination, otherwise the summation of the results would not so nearly equal one hundred per cent. Again, cupric oxide gives essentially identical results, whether analysed by reduction or by electrolysis. It must be remembered that while some of the copper used in the present series of researches came from Lake Superior, the greater part was prepared from "chemically pure" German cupric sulphate. Some unknown constant impurity may have vitiated all the preparations, but the present evidence seems to show that pure electrolytic copper is as definite a substance as most of the other "elementary substances" to which our atomic weights are referred.† A more elaborate comparison of copper from different sources and different modes of preparation would nevertheless be one of considerable interest.

V. SUMMARY OF RESULTS, 1887 to 1891.

The Atomic Weight of Copper.

O = 16.000.

Ratio.	Determinations	Result.
I. 2Ag : Cu	11	63.601
II. 2AgBr : Cu[Br ₂]	3	63.609
III. 2Ag : Cu[Br ₂]	3	63.605
IV. [CuSO ₄ —Cu] : Cu	3	63.593
V. Na ₂ CO ₃ : Cu	7	63.600
VI. Na ₂ SO ₄ : Cu	4	63.607
VII. Na ₂ CO ₃ : [CuSO ₄ —SO ₄]	2	63.621
VIII. Na ₂ SO ₄ : [CuSO ₄ —SO ₄]	3	63.641
IX. BaSO ₄ : Cu	1	63.603
X. BaSO ₄ : [CuSO ₄ —SO ₄]	1	63.625
XI. [CuO—Cu] corrected : Cu	5	63.604

General average of the eleven series 63.610

" " forty-three determinations 63.606

Of these results, five—namely, I., II., III., V., and VI.—are incomparably more trustworthy than the others. Their computation involves only very accurately determined elements, and they are least affected by a given

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

† Soré, *Compt. Rend.*, cviii., 733, cviii., 1298; Hampe, *loc. cit.*; also MacIntosh, Classen, Foote, Smith, and many others.

* *Ann. Chim. Phys.* [3], viii., 189, 205. See also Thudichum and Hake, *Jahresber.*, 1876, p. 966; and Johnson, *Jahresber.*, 1878, p. 286.

† Grünwald and Brauner have independently come to the conclusion that copper is a compound. If this is the case, the compound must be a very definite one. See *Chem. Soc. Abstracts*, 1890, p. 434.

change in the molecular weights of the standards of reference. Their experimental errors are far smaller than those of any of the others, and they involve the simplest and most direct processes, and the minimum number of necessary corrections. They are in no case computed by the objectionable method of difference. Finally, each one of the five is wholly independent of the weight of any copper compound whatsoever. These reasons constitute a sufficient ground for the separation of such results from the others.

Selected Series.

Ratio.	Salt decomposed.	If O = 16'000, Cu =
I. 2Ag : Cu	AgNO ₃	63'601
II. 2AgBr : Cu	CuBr ₂	63'609
III. 2Ag : Cu	CuBr ₂	63'605
V. Na ₂ CO ₃ : Cu	CuSO ₄	63'600
VI. Na ₂ SO ₄ : Cu	CuSO ₄	63'607

Final average 63'604

If the oxygen is taken as 15'96, copper becomes 63'44. With oxygen 15'87, the value sinks to 63'09.

The mathematical discussion of these results is omitted, because it gives an exaggerated notion of the accuracy of the final average. The real probable error of this average is much more dependent upon the chemical purity of the electrolytic copper than upon the mere mechanical or experimental error with which alone the theory of least squares is competent to deal.

It is apparent that any one of the methods thoroughly investigated would have long ago afforded a fairly accurate knowledge of the atomic weight. Too much cannot be said against the multiplication of incomplete or carelessly obtained data; for such data carry with them not only uncertainty and confusion in the present, but also additional labour for a reviser in the future.

In the present investigation every reaction was assumed to involve some constant error, and every substance was assumed to contain some constant impurity, until a proof of the contrary was obtained. The research consisted, in fact, of a succession of mutual checks. The attempt was made to adopt precautions of a consistent order of refinement; and the still remaining causes of possible error have been carefully pointed out in the description. The not inconsiderable outlay of time, thought, and labour has been more than repaid by a conviction of the definiteness of the combining proportions which four years ago would have seemed to the writer impossible.

CAN ARSENIC BE QUANTITATIVELY
VOLATILISED AS ARSENIC HYDRIDE?

By F. W. SCHMIDT.

(Concluded from p. 72).

To decide the correctness of this assumption there were introduced into the round flask of the apparatus described above, in addition to 30 grms. of pulverised zinc (zinc can be readily pulverised at 205°), 20 c.c. of a 1 per cent solution of arsenic containing 0'119 gm. of arsenic trioxide. (One gm. of commercial arsenious acid was dissolved in 100 c.c. of water; 20 c.c. of this solution consumed 40'2 c.c. decinormal iodine, corresponding to 0'199 gm. pure arsenic trioxide). The first absorption vessel was again charged with solution of silver 1 : 50, the second and the third with solution of silver at 1 : 10. After the apparatus was put together, hydrochloric acid (1 : 1) was again allowed to enter by means of the dropping-funnel as before, heat was applied until the zinc was entirely dissolved, and finally hydrogen free from arsenic was passed through the apparatus. The titration of the contents of

the absorption vessels (after precipitating the excess of silver by means of sodium chloride, &c.) used only 38'4 c.c. decinormal solution of iodine, which corresponds to 0'190 gm. arsenious acid; hence nearly 5 per cent of the original quantity of arsenic had remained in the round flask,—a result which confirms those formerly obtained by other authors.

Now came the decisive experiment, which was effected in the same manner with 20 c.c. of the 1 per cent solution of arsenic and 30 grms. of powdered zinc. When after heating for one hour the development of arsenic became sluggish, there was added to the contents of the round flask through the dropping-funnel an agent calculated to produce a state of the arsenic analogous to "combination or fine metallic distribution," i.e., a hydrochloric solution of stannous chloride (obtained by dissolving non-arseniferous tin foil in concentrated hydrochloric acid).

At the moment when this solution was dropped into the round flask there appeared at once a turbidity and then a dark precipitation. Both the turbidity and the precipitate disappeared in a few minutes after a little platinum chloride had been added to re-animate the development of hydrogen, and the liquid resumed its former appearance. The application of heat was still continued for about 15 minutes, and a current of hydrogen free from arsenic was then passed through the apparatus for about the same time. The titration of the contents of the absorption vessels then showed exactly 0'119 gm. of arsenious acid, since 40'2 c.c. of decinormal iodine solution were required for its conversion into arsenic acid. The residue in the round flask, on careful examination, showed no trace of an arsenical reaction.

Hence it follows with great probability that the above assumption is correct, though it is conceivable that the stannous chloride, in addition to its property of precipitating arsenic in a very finely-divided metallic condition, has also a catalytic action, since stannous chloride is continually regenerated in the liquid. Its *modus operandi* is further explained by the following observations. After proceeding as usual, and as the zinc in the round flask was chiefly dissolved, solution of stannous chloride containing 1 or 2 grms. of metallic tin was allowed to flow slowly in through the dropping funnel. The tin was by degrees rather quickly separated out as a spongy mass, which dissolved only slowly on the addition of concentrated hydrochloric acid, but could be easily dissolved with a brisk escape of hydrogen on the addition of a little platinum chloride. These spongy masses were taken out of the liquid for closer examination and washed in distilled water. It was then found that they had taken up the main part of the arsenic present in the liquid which retained only traces. Whether in this case the arsenic as separated really combines with the tin as tin arsenide, or if the arsenic remains in the spongy tin in a state of fine metallic division, must be left undecided.

In a check experiment the following conditions were observed. As working with the apparatus above described offers the inconvenience that the addition of liquids into the hot round flask through the dropping funnel can be effected only with the utmost caution, in order to avoid a reflux occasioned by the momentary cooling, there was inserted after the round flask, containing now 300 c.c. of materials, a Woulf's bottle, holding 150 c.c., the gas introductory tube of which was provided with a Bunsen valve or a glass ball valve. Thus a reflux was rendered impossible, and it was no longer necessary to observe the working of the apparatus. The Woulf's bottle was now connected with three receivers each of the capacity of 100 c.c.; all contained silver solution 1 : 50, and the Woulf's bottle as much as corresponded to the arsenic used in the experiment.

The precaution was also employed that all the liquids could be forced into the round flask by a pressure of hydrogen, whereby any ascent of gas bubbles in the dropping flask was at once excluded.

Since the zinc used (not the same as that used in the

former experiments, which had all been consumed) was found on careful examination to contain a minimum trace of zinc, this trace was first determined in the apparatus. 30 grms. of the zinc were found to contain 0.00375 per cent of arsenic, corresponding to 0.3 c.c. of the decinormal solution of iodine, which was consumed on titrating the contents of the receivers. If, therefore, again 20 c.c. of the 1 per cent solution of arsenic, which required as before on titration 40.2 c.c. of decinormal solution of iodine, were volatilised in the apparatus as arsenic hydride by means of 30 grms. of zinc, the titration of the contents of the receivers after elimination of the excess of silver, &c., must show an excess of 0.3 c.c. of the standard liquid. This was, in fact, the case. On titration there were consumed 40.47 c.c., consequently there were found 40.17 c.c. of the decinormal solution. Thus the availability of the method was demonstrated.

Further experiments are intended, and the method will be especially tested to find whether it may be ultimately available for a separation of arsenic from antimony, or for the determination of both elements when simultaneously present. Whilst arsenic hydride reacts with a dilute silver solution to form arsenious acid, and to liberate metallic silver, antimony hydride precipitates from a solution of silver, even if its concentration is only 1:80, merely black silver antimonide, upon which behaviour the separation of both elements may possibly be based.

This profound difference in the behaviour of both hydrogen compounds with dilute solutions of silver is also theoretically interesting. If we reflect that in the oxygen compounds of the trivalent elements, N, P, As, Sb, consequently in N_2O_3 , P_2O_3 , As_2O_3 , Sb_2O_3 , the acid character continually decreases, and that with higher atomic weights basic characters become more perceptible, and that in the corresponding hydrogen compounds, NH_3 , PH_3 , AsH_3 , SbH_3 , the behaviour is exactly the reverse, we are inclined to ascribe to antimony hydride faintly acid properties which come clearly into evidence in their action upon dilute silver solutions. For the recognition of antimony hydride as a feeble acid—feeblar than sulphuretted hydrogen—we have the testimony of the occurrence in nature of silver antimonide, whilst silver arsenide is known neither chemically nor as a mineral.

The above described method is a simple means for the determination of arsenic, and is the more important in toxicology, as in forensic inquiries arsenic is almost exclusively recognised by the Marsh test.

CORRESPONDENCE.

ESTIMATION OF CAOUTCHOUC.

To the Editor of the Chemical News.

SIR,—I should like to know how your correspondent, Mr. Phillips, estimated the amount of caoutchouc in his analysis of an indiarubber mat, and how he proved conclusively the absence of an indiarubber substitute. I have been connected with the trade some years, and during the whole of my experience I have never seen or heard of a mat being made of 50 per cent pure caoutchouc, —its price would be prohibitive.—I am, &c.,

PERCY CARTER BELL, F.I.C., F.C.S.

34, Poulton Rd., Fleetwood,
August 8, 1892.

New Derivatives of Amethylcamphonitroketone.—P. Cazeneuve.—The author describes the sodium-, the ethyl-, and sodium-ethyl, the acetyl- and sodium-ethyl derivatives.—*Bull. de la Soc. Chim. de Paris*, Series 3, vii.—viii., No. 11.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

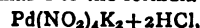
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 2, July 11, 1892.

Determination of the Density of Gases.—Henri Moissan and Henri Gautier.—This paper requires the two accompanying figures.

The Alkoylcyanocamphors and the Benzeneazocamphocarbonic Ethers.—A. Haller.—An account of the benzeneazocamphocarbonic ethers, and especially of the methyl- and ethyl-benzeneazocamphocarbonates.

A Palladium Chloronitrate.—M. Vèzes.—The composition of this compound answers to the formula $Pd(NO_2)_2Cl_2K$. It may be prepared by the limited action of hydrochloric acid upon potassium palladionitrite in proportion conformable to the formula—



or by the limited action of potassium nitrite upon potassium chloropalladite, or by the action of potassium chloropalladite upon potassium palladionitrite in equivalent proportions. It is unalterable in air, and does not lose water at 100°. At dull redness it is decomposed with production of nitrous vapours, leaving a residue of palladium and potassium chloride. It is soluble in about three times its weight of cold water and twice its weight of boiling water.

Double Chlorides formed by Lithium Chloride and Chlorides of the Magnesian Series.—A. Chassevant.—The author has obtained four chlorides formed by combining lithium chloride with manganese, iron, cobalt, and nickel chlorides. These compounds have all a formula corresponding to the formula $2MCl.LiCl.6HO$. They all contain the same quantity of crystalline water. They are all easily dissociable into their elements by water, but stable in presence of an excess of one of their components, lithium chloride. They have the colour of the anhydrous chloride of the metal which enters into their composition. Thus the double chloride of nickel and lithium is yellow, and that of the double chloride of cobalt and nickel is blue. Heat decomposes them, forming either an oxychloride or an oxide of the metal which enters into their composition. They are all efflorescent in a dry atmosphere, and in these conditions lose hydrochloric acid. They are isomorphous.

Researches on Nickel and Cobalt.—Ch. Leprieux and M. Lachaud.—In a former communication the authors describe the action of ammonium bisulphate upon the salts of iron. They now describe the new substances obtained with nickel and cobalt. The series of compounds obtained with nickel and cobalt are analogous to those of iron, though less complete.

On the Quinine Iodomethylates.—E. Grimaux.—Quinine, $C_{20}H_{24}N_2O_8$, may be considered as formed of two groups, one approximating to quinoline, and the other probably of pyridic or piperidic character. It constitutes a diacid base, which may be united to 1 or 2 mols. of monobasic acids, or may combine with 1 mol. or 2 mols. of methyl iodide to form moniodomethylate or diiodomethylates. The author, whilst studying the action of alkalis upon iodomethylates in the cold, has determined upon which of the atoms of nitrogen in quinine the first mol. of CH_3I is fixed in the formation of iodomethylates.

On Methylated Camphocarbonic Ethers, Methylcamphor, and certain Nitrogen Derivatives of Cyanocamphor.—J. Minguin.—Not suitable for abstraction.

Action of Non-Metallic Nitrides and Hydronitrides upon the Oxyhydrocarbonic Compounds.—R. Vidal. —The author has obtained the naphthol β , a product which represents the same centesimal composition as the dinaphthylamines, but it differs by its physical and chemical characters. It melts only at 225° and does not combine with acids.

Certain Ferruginous Medicines.—H. Le Chatelier. —The author holds that it is practically impossible to find in commerce at Paris so-called chalybeate waters which contain a notable quantity of iron. Certain of these waters contained it regularly twenty years ago.

Contributions to the Study of Mineral Waters; on Alumina contained in Waters.—F. Parmentier. —The authors have found alumina in all natural waters, mineral or others, which they have analysed. They have also found alumina in notable quantities in springs formerly studied, though the published analyses do not mention it.

Respiratory Value of Hæmocyanine.—L. Cuenot. —In blood containing hæmocyanine the blood is capable of absorbing more oxygen than an equal volume of water, but its absorbent power for oxygen is very feeble compared with the hæmoglobine of the vertebrates. The author throws doubts on the experiments of Dr. Griffiths.

Physiological Action of Spermine. Interpretation of its Effects on the Organism.—Alexandre Poehl. —The author assigns to pure spermine the formula $C_5H_{14}N_2$.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) of the Edinburgh Meeting of the British Association:—

President—Professor Herbert McLeod, F.R.S., F.C.S.

Vice-Presidents—Professor A. Crum Brown, M.D., D.Sc., F.R.S., F.R.S.E., Pres. C.S.; J. H. Gladstone, Ph.D., F.R.S.; Professor F. R. Japp, M.A., Ph.D., LL.D., F.R.S., F.C.S.; Professor W. H. Perkin, jun., Ph.D., F.R.S., F.R.S.E., F.C.S.; Professor Otto Petersen; Professor T. Purdie, Ph.D., B.Sc., F.C.S.; Professor J. Emerson Reynolds, M.D., D.Sc., F.R.S., F.C.S., M.R.I.A.; Professor W. C. Roberts-Austen, C.B., F.R.S., F.C.S.

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The Papers brought before the Section were as follows:—

President's Address.

Professor Crum Brown, F.R.S., and Dr. J. Walker.—Electrolytic Synthesis.

Professor W. Ramsay, F.R.S.—Impurities in Chloroform.

Report of the Committee on the Properties of Solutions.

Report of the Committee on the Bibliography of Solution.

Report of the Committee on Wave-length Spectra of the Elements.

T. W. Hogg.—Some Alloys of Iron, Manganese, and Aluminium.

B. Lean and W. A. Bone.—The Explosion of Ethylene with less than its own volume of Oxygen.

Prof. V. B. Lewis.—Luminosity of Hydrocarbon Flames.

Prof. A. Smithells.—Experiments on Flame.

Report of the Committee on the direct formation of Haloids from Pure Materials.

Dr. J. A. Harker.—The Reaction of Hydrogen with Mixtures of Oxygen and Chlorine.

Prof. W. R. Hodgkinson and Col. Trench.—Action of Dry Ammonia on Sulphates.

Prof. W. R. Hodgkinson and J. Young.—Action of Dry Sulphur Dioxide on Oxy-salts.

Prof. F. Clowes.—The application of a Hydrogen Flame in the Safety Lamp to the Detection and Estimation of Inflammable Gases and Vapours in Air.

Report of the Committee on the Influence of the Silent Discharge of Electricity on Oxygen and other Gases.

Report of the Committee appointed to consider the best Method of Establishing an International Standard for the Analysis of Iron and Steel.

Dr. J. H. Gladstone, F.R.S.—Notes on the Molecular Refraction and Dispersion of (a) Metallic Carbonyls, (b) Indium and Gallium, (c) Sulphur.

Prof. W. C. Roberts-Austen, F.R.S.—The Effect of Small Quantities of Foreign Matter on the Properties of Metals.

Dr. Svante Arrhenius.—Researches on Diffusion.

Prof. W. Ramsay, F.R.S.—The Transpiration of Hydrogen through Palladium.

Dr. G. H. Bailey.—The Impurities of Town Air.

Prof. W. H. Perkin, jun., F.R.S.—Syntheses with the aid of Butane and Pentane Tetra-carboxylic Ethers.

Dr. F. Stanley Kipping.—Synthesis of Hydrindone Derivatives.

Dr. F. Stanley Kipping.—Heptamethylene Derivatives.

Dr. F. Stanley Kipping.—Action of Phosphoric Anhydride on Fatty Acids.

Dr. J. Walker.—Methyl Salts of Camphoric Acid.

Dr. L. Dobbin and Dr. J. Walker.—Halogen Addition Products of Salts of Organic Bases.

J. F. Isaac.—The Production of Acetic Acid from the Carbohydrates.

Dr. W. W. J. Nicol.—The Molecular Volumes of Organic Compounds in Dilute Solution.

Report of the Committee on Isomeric Naphthalene Derivatives.

Report of the Committee on the Action of Light on Dyed Colours.

Dr. Shields.—On the amount of Hydrolysis in Aqueous Solutions of Salts of Strong Bases with Weak Acids.

B. Lean and W. A. Bone.—A new Method of Measuring the Pressure produced in Gaseous Explosions.

Dr. F. E. Matthews.—The Determination of Small Quantities of Nitrogen in Soils.

Dr. J. J. Kyla.—A Vanadiferous Lignite.

G. Carrington Purves.—Sewage Precipitation.

Prof. W. Ramsay, F.R.S., and Emily Aston.—The Atomic Weight of Boron.

Dr. J. Gibson.—Preparation of Pure Glucina and the Atomic Weight of Glucinum.

Dr. J. Gibson.—Note on Exact Weighing.

Dr. J. Gibson.—Analysis of Manganese Nodules.

Prof. W. Ostwald.—On the Assumed Potential Difference between Metals in the Solid and in the Molten State.

Prof. H. M'Leod, F.R.S.—Iodides of Sulphur.

Dr. W. W. J. Nicol.—Solutions of Iodine.

Dr. H. Marshall.—Persulphates.

Dr. H. Marshall.—Cobaltic Salts.

Report of the Committee on the Bibliography of Spectroscopy.

Report of the Committee on the Action of Light on the Hydracids of the Halogens in presence of Oxygen.

Report of the Committee on the Proximate Constituents of Coal.

W. Durham.—Note on Valency and Atomicity.

Thos. Ewan and W. R. Ormandy.—On a Method for Determining the Vapour Pressures of Solutions.

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Edited by
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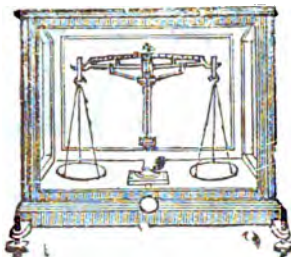
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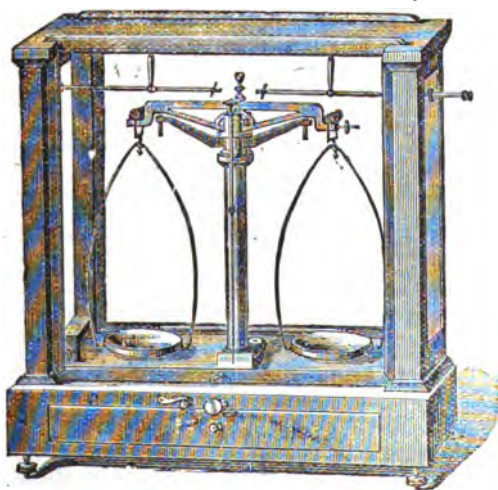


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ADDRESS TO THE MATHEMATICAL AND PHYSICAL SECTION OF THE BRITISH ASSOCIATION, EDINBURGH, 1892.

By Prof. ARTHUR SCHUSTER, Ph.D., F.R.S., F.R.A.S.,
President of the Section.

(Concluded from p. 81).

ONE of the principal obstacles to the rapid diffusion of a new idea lies in the difficulty of finding suitable expressions to convey its essential point to other minds. Words may have to be strained into a new sense, and scientific controversies constantly resolve themselves into differences about the meaning of words. On the other hand, a happy nomenclature has sometimes been more powerful than rigorous logic in allowing a new train of thought to be quickly and generally accepted.

A good example is furnished by the history of the science of energy. The principle of the conservation of energy has undoubtedly gained a more rapid and general acceptance than it would otherwise have had by the introduction of the word potential energy. A great theorem, which in itself seems to me to be an intricate one, has been simplified by calling something energy which, in the first place, is only a deficiency of kinetic energy. The only record I can find on the history of the expression is given in Tait's "Thermodynamics," wherein the term statical energy is ascribed to Lord Kelvin, and that of potential energy to Rankine. It would be of interest to have a more detailed account on the origin of an expression which has undoubtedly had a marked influence not only on the physics, but also on the metaphysics of our time. But while fully recognising the very great advantage we have derived from this term "Potential Energy," we ought not, at the same time, to lose sight of the fact that it implies something more than can be said to be proved. It is easy to overstep the legitimate use of the word. Thus, when Professor Lodge (*Phil. Mag.*, xi., p. 36, 1881) attempts to prove that action at a distance is not consistent with the doctrine of energy, he cannot, in my opinion, justify his position except by assuming that all energy is ultimately kinetic. That is a plausible, but by no means a necessary theory. Efforts have been made to look on energy as on something which can be labelled and identified through its various transformations. Thus we may feel a certain bit of energy radiating from a coal fire, and if our knowledge was complete, we ought to be able to fix the time at which that identical bit of energy left the sun and arrived on the surface of the earth, setting up a chemical action in the leaves of the plant from which the coal has been derived. If we push this view to a logical conclusion, it seems to me that we must finally arrive at an atomic conception of energy which some may consider an absurdity.

Let, for instance, a number of particles $P_1, P_2, \&c.$, in succession, strike another particle Q . How can we in the translatory energy of the latter identify the parts which $P_1, P_2, \&c.$, have contributed? According to Professor Lodge's view, we should be able to do so, for if the particle Q in its turn gives up its energy to others, say $R_1, R_2, R_3, \&c.$, we ought to be able to say whether the energy of P_1 has ultimately gone into R_1 or into R_2 , or is divided between them. It is only by imagining that all energy is made up of a finite number of bits, which

pass from one body to another, that we can defend the idea of considering energy as capable of being "labelled."

In the expressions we adopt to describe physical phenomena we necessarily hover between two extremes. We either have to choose a word which implies more than we can prove, or we have to use vague and general terms which hide the essential point, instead of bringing it out. The history of electrical theories furnishes a good example. The terms positive and negative electricity committed us to something definite; we could reckon about quantities of electricity, and form some definite notion of electrical currents as a motion of the two kinds of electricity in opposite directions. Now we have changed all that; we speak of electric displacements, but safeguard ourselves by saying that a displacement only means a vector quantity, and not necessarily an actual displacement. We speak of lines and tubes of force not only as a help to realise more clearly certain analytical results, but as implying a physical theory to which, at the same time, we do not wish to commit ourselves. I do not find any fault with this, for it is a perfectly legitimate and necessary process to state the known connection between physical phenomena in some form which introduces the smallest number of assumptions. But the great question "What is electricity?" is not touched by these general considerations. The brilliant success with which Maxwell's investigations have been crowned is apt to make us overrate the progress made in the solution of that question. Maxwell and his followers have proved the important fact that optical and electrical actions are transmitted through the same medium. We may be said to have arrived in the subject of electricity at the stage at which optics was placed before Young and Fresnel hit on the idea of transverse vibrations, but there is no theory of electricity in the sense in which there is an elastic solid theory of light.

If the term electrical displacement was taken in its literal sense, it would mean that the electric current consists of the motion of the ether through the conductor. This is a plausible hypothesis, and one respecting which we may obtain experimental evidence. The experiments of Rayleigh and others have shown that the velocity of light in an electrolyte, through which an electric current is passing, is, within experimental limits, the same with and against the current. This result shows that if an electrical current means a motion of the ether the velocity of the medium cannot exceed ten metres a second for a current density of one ampère per square centimetre. This, then, is the upper limit for a possible velocity of the medium; can we find a lower limit? The answer to that question depends on the interpretation of a well-known experiment of Fizeau's, who found that the speed of light is increased if it travels through water which moves in the same direction as the light. If this experiment implies that the water carries the ether with it, and if a motion of the ether means an electric current, we should be led to the conclusion that a current of water should deflect a magnet in its neighbourhood. An experiment made to that effect would almost certainly give a negative result, and would give us a lower limit for the velocity of the medium corresponding to a given current. Such an experiment, together with that of Rayleigh, would probably dispose of the theory that an electric current is due to a translatory velocity of the medium. This would be an important step, and it would be worth while to arrive at a final settlement of the question.* The whole question of the relation between the motion of matter and the motion of the medium is a vital one, and we shall probably not make any serious advances until experiment

* Fizeau's result must either be due to the motion of matter through the medium or to the fact that moving matter carries the ether with it. If it is due to the former cause, and matter does *not* carry the ether with it, may we not consider that matter moving through the ether, that is a relative motion of matter and ether, must produce effects equal and opposite to those of ether moving through matter? In that case the reasoning in the text would, *mutatis mutandis*, hold good.

has found a new opening. But we must expect many negative results before some clue is discovered. Nor can we attach much importance to negative results unless they are made by someone in whose care and judgment we place full reliance. We should all the more, therefore, recognise the courage and perseverance of those who spend their valuable time in such investigations as Professor Lodge has recently undertaken. That ultimately some relation will be found between moving matter and electrical action there is no reasonable doubt.

One of the most hopeful openings for new investigations has always been found in the pursuing of a theory to its logical conclusions, and there is one result of the electromagnetic theory of light which has not, in my opinion, received the share of attention which it deserves.

When sound passes through air it is propagated more quickly with the wind than against it, and we may easily find the velocity relative to the earth by combining the ordinary sound velocity with the velocity of the wind. Similarly, when any waves pass through a medium moving with uniform velocity, the waves being due to internal stresses in the medium, we may treat of the velocity of the waves independently of that of the medium, and say that the wave-velocity in the direction of motion of the medium, and relative to a fixed body, is the sum of the wave-velocity calculated on the supposition that the medium is at rest and the velocity of the medium. Professor J. J. Thomson (*Phil. Mag.*, vol. ix., p. 284, 1880), applying Maxwell's equations, has arrived at a different result for electromagnetic waves, and has come to the conclusion that in order to get the velocity of light along a stream of flowing water, we have to add to the velocity of light only half the velocity of water. The following considerations suggest themselves to me with respect to this result. Maxwell's theory is founded on certain observed effects, which all depend on the relative motion of matter. A result such as the one referred to implies actions depending on absolute motion, and appears therefore to point to something which has been introduced into the equations for which there is no experimental evidence. The only assumption clearly put down by Maxwell is that electromagnetic actions are transmitted through the medium, and it is possible that that assumption necessarily carries Prof. J. J. Thomson's result with it. If a careful examination of the subject should show that this is the case, we are brought face to face with a serious difficulty. It is said, with justice, to be one of the great advantages of Maxwell's theory that it does away with action at a distance; but what do we gain if we replace action at a distance by something infinitely more difficult to conceive, namely, internal stresses of a medium depending on the velocity of the medium through space? I can only see one loophole through which to escape, namely, that Maxwell's medium is not homogeneous, but consists of two parts, and that if we speak of the medium as moving, we mean the motion of one of these parts relative to the other.

While we may hope to obtain important results from an investigation of the relation between what we call electricity and the medium, we must not lose sight of another avenue, namely, the relation between electricity and chemical effects. The passage of electricity through gases presents us with a complicated problem to which a number of physicists have given their attention of late years. There seems no reasonable doubt that electricity in a gas is conveyed by the diffusion of particles conveying high charges, probably identical with those carried by the electrolytic ion. The fact that this convection is a process of diffusion with comparatively small velocity is shown by the experimental result that the path of the discharge is affected by any bodily motion of the gas which conveys the current. Even the convection currents due to the heat produced by the discharge itself are sufficient to deflect the luminous column which marks the passage of the current.

The most puzzling fact, however, connected with the

discharge of electricity through gases consists in the absence of symmetry at the positive and negative poles. There must be some difference between a positively and negatively charged atom which seems of fundamental importance in the relation between matter and what we call electricity. A discussion of the various phenomena attending the discharge of electricity through gases seems to me to point to a conclusion which may possibly prove a step in the right direction.

A surface of separation between bodies having different conductivities becomes electrified by the passage of a current, while at the surface between two chemically distinct bodies we have, according to Helmholtz, a sheet covered at the two sides with opposite electricities. These surface electrifications are not merely imaginary layers invented to satisfy mathematical surface conditions. They can be proved to be realities. Thus, when one electrolyte floats on another, the specific resistances being different, we often observe secondary chemical effects due to the action of the ions which carry the surface electrification.

If the passage of electricity from the solid to the gas involves some work done, we must expect a double sheet of electricity at the boundary, the gas in contact with the kathode becoming positively, and that in contact with the anode negatively, electrified. *A priori* we can form no idea how a layer of gas, the atoms of which carry charges, will behave. The ordinary proof that all electrification must be confined to the surface implies that all forces act according to the law of the inverse square, but where we have also to consider molecular forces, I see no reason why the electrification at a surface may not stretch across a layer having a thickness comparable with the mean free path of the molecule. It is here that there seems to be the fundamental difference between positive and negative electricity. A negative electrification of the gas, like that of a solid or a liquid, seems always confined to the surface, and no one has ever observed a volume electrification of negative electricity. The case is different for the positively electrified part of the gas. Wherever from other considerations we should expect a positively electrified surface sheet, we always get a layer of finite thickness. The result implies a different law of impact between positively and negatively electrified ions, but I see no inherent improbability in this. That the kathode jet into a gas is surrounded by a positively electrified layer of finite thickness extending outwards must be considered as an established fact, and several of the characteristic features of the discharge are explained by it. The large fall of potential at the kathode can also be explained on the view which I have put forward, for in order to keep up the discharge there must be a sufficient normal force at the surface, and if this force is not confined to the surface, but necessarily stretches across a finite layer, the fall of potential must be multiplied a great number of times. Similarly Goldstein has shown that some of the phenomena of the kathode are observed at every place at which the positive current flows from a wide to a narrow part of a column of gas. At such places we should expect a positive surface electrification, and here, again, the whole appearance tends to show that we are dealing with a positive volume electrification. No corresponding phenomena are observed when the current passes from the narrow to the wide part.

The fact that in all cases experimented upon positive volume electrifications are observed, but never similar negative electrifications, is surely of significance.

Some of the results recently brought to light by investigations on the discharge of electricity have interesting cosmical applications. Thus it is found that such a discharge through any part of a vessel containing a gas converts the whole gas into a conductor.* The dissoci-

* An experiment by Hittorf (*Wied. Ann.*, vii., p. 614), suggested the probability of this fact, which was proved independently by Arrhenius and myself.

tion which we imagine to take place in a liquid before electrolytic conduction takes place must be artificially produced in a gas by the discharge itself. We may imitate in gases which have thus been rendered conductive many of the phenomena hitherto restricted to liquids; thus I hope to bring to the notice of this meeting cases of primary and secondary cells in which the electrolyte is a gas. There are other ways in which a gas can be put into that sensitive state in which we may treat it as a conductor, and we have every reason to suppose that the upper regions of our atmosphere are in this state. The principal part of the daily variation of the magnetic needle is due to causes lying outside the surface of the earth, and is in all probability only an electro-magnetic effect due to that bodily motion in our atmosphere which shows itself in the diurnal changes of the barometer. A favourite idea of the late Prof. Balfour Stewart will thus probably be confirmed. The difference in the diurnal range between times of maximum and times of minimum sun-spots is accounted for by the fact that the atmosphere is a better conductor at times of maximum sun-spots.

The mention of sun-spots raises a point not altogether new to this section. Careful observations of celestial phenomena may suggest to us the solution of many mysteries which are now puzzling us. Consider, for instance, how long it would have taken to prove the universal property of gravitational attraction if the record of planetary motion had not come to the philosopher's help. And surely the most casual observation of cosmical effects teaches us how much we have yet to learn.

The statement of a problem occasionally helps to clear it up, and I may be allowed, therefore, to put before you some questions, the solution of which seems not beyond the reach of our powers.

1. Is every large rotating mass a magnet? If it is, the sun must be a powerful magnet. The comets' tails, which eclipse observations show stretching out from our sun in all directions, probably consist of electric discharges. The effect of a magnet on the discharge is known, and careful investigations of the streamers of the solar corona ought to give an answer to the question which I have put.*

2. Is there sufficient matter in interplanetary space to make it a conductor of electricity? I believe the evidence to be in favour of that view. But the conductivity can only be small, for otherwise the earth would gradually set itself to revolve about its magnetic pole. Suppose the electric resistance of interplanetary space to be so great that no appreciable change in the earth's axis of rotation could have taken place within historical times, is it not possible that the currents induced in planetary space by the earth's revolution may, by their electromagnetic action, cause the secular variation of terrestrial magnetism? There seems to me to be here a definite question capable of a definite answer, and as far as I can judge, without a strict mathematical investigation, the answer is in the affirmative.

3. What is a sun-spot? It is, I believe, generally assumed that it is analogous to one of our cyclones. The general appearance of a sun-spot does not show any marked cyclonic motion, though what we see is really determined by the distribution of temperature and not by the lines of flow. But a number of cyclones clustering together like the sun-spots in a group should move round each other in a definite way, and it seems to me that the close study of the relative positions of a group of spots should give decisive evidence for or against the cyclone theory.

4. If the spot is not due to cyclonic motion, is it not possible that electric discharges setting out from the sun,

and accelerating artificially evaporation at the sun's surface, might cool those parts from which the discharge starts and thus produce a sun-spot? The effects of electric discharges on matters of solar physics have already been discussed by Dr. Huggins.

5. May not the periodicity of sun-spots, and the connection between two such dissimilar phenomena as spots on the sun and magnetic disturbances on the earth, be due to a periodically recurring increase in the electric conductivity of the parts of space surrounding the sun? Such an increase of conductivity might be produced by meteoric matter circulating round the sun.

6. What causes the anomalous law of rotation of the solar photosphere? It has long been known that groups of spots at the solar equator perform their revolution in a shorter time than those in a higher latitude; but spots are disturbances which may have their own proper motions. Duner* has shown, however, from the displacement of the Fraunhofer lines, that the whole of the layer which produces these lines follows the same anomalous law, the angular velocity at a latitude of 75° being 30 per cent less than near the equator.† As all causes acting within the sun might cause the angular velocity of the sun to be smaller at the equator than at other latitudes, but could not make it greater, the only explanation open to us is an outside effect either by an influx of meteoric matter, as suggested by Lord Kelvin, or in some other way. If we are to trust Dr. Welsing's result, that faculæ which have their seat below the photosphere revolve in all latitudes with the same velocity, which is that of the spot velocity in the equatorial region, we should have to find a cause for a retardation in higher latitudes rather than for an acceleration at the equator. The exceptional behaviour of the solar surface seems to me to deserve very careful attention from solar physicists. Its explanation will probably carry with it that of many other phenomena.

In conclusion, I should like to return for an instant to the question whether it is possible by any means to render the progress of science more smooth and swift. If there is any truth in the idea that two types of mind are necessary, the one corresponding to the boiler and the other to the cooler of a steam engine, it must also be true that some place must be found where the two may bring their influence to bear on each other. I venture to think that no better ground can be chosen than that supplied by our meetings. We hear it said that the British Association has fulfilled its object; we are told that it was originally founded to create a general interest in scientific problems in the towns in which it meets; and now that popular lectures and popular literature are supposed to perform that work more satisfactorily, we are politely asked to commit the happy despatch. There is no need to go back to the original intention of those who have founded this institution, which has at any rate adapted itself sufficiently well to the altered circumstances to maintain a beneficial influence in scientific research.

The free discussion which takes place in our sections, the interchange of ideas between men who during the rest of the year have occupied their minds, perhaps too much, with some special problem, the personal intercourse between those who are beginning their work with sanguine expectations, and those who have lost the first freshness of their enthusiasm, should surely one and all ensure a long prosperity to our meetings. If we cannot claim any longer to sow the seeds of scientific interest in the towns we visit, because the interest is established, we can at any rate assure those who so kindly offer us hospitality, that they are helping powerfully in the promotion of the great object which we all have at heart.

* "Oefvers. af Kongl. Vetensk. Ak. Forhandl.," p. 47, 1890.

† Although the importance of M. Duner's results would make an independent investigation desirable, the measurements of Mr. Crew, who by a much inferior method arrived at other results, cannot have much weight as compared with those of Duner.

* The efforts of Mr. Bigelow have a bearing on this point, also some remarks which I have made in a lecture before the Royal Institution (*Proc. Roy. Inst.*, 1891), but nothing decisive can be asserted at present.

VOLUMETRIC DETERMINATION OF
MERCURY.

By ROD. NAMIAS.

The volumetric process to be explained is applicable only to mercuric chloride, into which every other compound must be previously converted. The nitrate must be treated with hydrochloric acid in excess, and evaporated to dryness; the mercurous salts are submitted to evaporation in presence of hydrochloric acid and of potassium chlorate.

The evaporation must be conducted with care at a temperature below that of ebullition, so as to avoid any loss of mercuric chloride by volatilisation.

The process depends upon the following principle:—If to a solution of mercuric chloride, slightly acidified with hydrochloric acid, we add a solution of stannous chloride, the mercuric chloride is reduced first to the mercurous state and then to metallic mercury. But whilst the first reaction is nearly instantaneous, the second takes a longer or shorter time, so much the longer as the excess of the stannous chloride is less.

If we have a reagent by which we can recognise the moment when the stannous chloride is in excess for the first reaction, and begins to produce the second, we may by this means determine the mercury volumetrically.

The reagent for detecting the presence of stannous chloride in excess is sodium molybdate. I dissolve a small quantity of molybdic anhydride in a solution of sodium hydrate or carbonate; I steep in this liquid a morsel of filter-paper, which I spread out whilst wet upon a plate of porcelain. The solution of molybdate ought to be freshly prepared, and the paper of good quality; it must not take a yellow tint on immersion in the alkaline liquid. The paper must be steeped in the molybdate only a little time before the experiment, so that it may not have time to dry.

The paper thus prepared shows a relatively slight excess of stannous chloride, which communicates to it according to its quantity a colour varying from the lightest sky-blue to an intense blue. This colour is due to the reduction of the molybdic acid. Ammonium molybdate, less stable than sodium molybdate, is less fit for use.

The determination of the value of the stannous solution may be made by means of a standard solution of iodine; but it is preferably effected by operating upon a known quantity of pure mercuric chloride obtained by sublimation.

If we operate with iodine we obtain a slight error in excess due to the small quantity of stannous chloride, which must be used in excess to mark the end of the operation by spotting upon the molybdate paper. In any case it is well to determine the standard of the stannous solution by means of iodine approximately, if not exactly; this serves as a control, and facilitates at the same time the exact titration by means of mercuric chloride.

To prepare the solution of stannous chloride I dissolve 2 to 3 grms. tin by means of hydrochloric acid, and dilute it to 1 litre. This solution is preserved in an apparatus which prevents alteration by contact with air. I determine its strength as follows:—0.2 to 0.4 grm. of mercuric chloride weighed exactly are dissolved in 50 c.c. of distilled water, and acidulated with $\frac{1}{4}$ c.c. of concentrated hydrochloric acid. Into this cold solution the stannous solution is allowed to flow from a burette. If the determination of the standard has been previously made with iodine, we may pour in at once, without fear of overstepping the limit, the volume as determined by calculation from the titration with iodine; we then add the liquid drop by drop, stirring carefully, and each time putting a drop of the mixture with the stirring-rod upon the molybdate paper. An excess of a few drops of the stannous liquid turns the paper to a pale blue, which be-

comes manifest after a few seconds, and which an experienced eye easily recognises.

To obtain a well-marked colouration, it is necessary to use an excess of from 0.3 to 0.5 c.c. for 50 c.c. of liquid. The small quantity of mercurous chloride placed upon the molybdate paper whilst "spotting" has no injurious influence upon the result.

The proportion of free hydrochloric acid contained in the liquid should be about 0.5 c.c. to 50 c.c. of the liquid; a larger proportion may occasion errors from its action upon the molybdic acid in presence of filter-paper.

To obtain exact results we must operate each time exactly as when standardising the liquid. We must, as far as possible, operate upon the same volume of liquid, in presence of the same proportion of hydrochloric acid, and obtain spots of the same intensity upon the molybdate paper.—*Revue Universelle des Mines.*

ANALYSIS OF COPAL RESINS.

By ED. KRESSEL.

Of all copals Zanzibar copal is the only one entirely free from taste and aroma; all other kinds possess more or less aroma, and some of these (Borneo and Manilla copal) a bitter aromatic taste. According to Brissou the specific gravity varies from 1.045 to 1.139, but in these estimations the air enclosed in the copal has not been regarded. The melting-point of a copal resin depends upon the hardness; the harder the resin the higher the melting-point. Andés gives the following average scale for hardness, which I have found to be correct:—

"Zanzibar, Sierra Leone, Angola, Benguela, Accra, Benin, Loango, Kauri, Manilla, Borneo, Singapore."

A good, hard, nearly colourless copal dried for some time over H_2SO_4 gave:—

	I.	II.	Average.
C	78.87	79.37	79.12
H	9.95	10.18	10.065
O	11.18	10.45	10.815
	100.00	100.00	100.00

With benzol, chloroform, disulphide of carbon, or ether, the powdered resin swells considerably; on putting to rest, a gelatinous mass will separate from the solution, which remains clear on top. I used freshly distilled ether entirely free of water as a solvent. I repeated the extraction of the resin with ether, until a few drops left little or no residue on evaporation. The substance insoluble in ether requires some considerable time to dry and to become of constant weight, and when so, it appears like horn. It is called "swell copal," as it only swells in every solvent and does not go into a clear solution. I found the amount of swell copal to be in proportion to the hardness of the raw copal resin. The copal now in question contained about 64.5 per cent of swell copal. Owing to the nature of this substance, copal resins cannot be used for varnishes in their raw state, but on heating it to a high temperature it is converted into pyro swell copal, which is easily soluble in any solvent.

The analysis of swell copal gave:—

	I.	II.	Average.
C	78.63	79.85	79.24
H	11.29	10.75	11.02
O	10.08	9.40	9.74
	100.00	100.00	100.00

The ether extraction of the raw copal leaves on distilling off the ether a light yellow resin, which is soft and remains so when even subjected to 100° C. for some time. On distillation, an oil goes over at about 132° C., leaving a brown brittle resin.

The substance dried by 130° C. gives :—

	I.	II.	Average.
C	78.60	78.40	78.50
H	10.25	10.35	10.30
O	11.15	11.25	11.20
	100.00	100.00	100.00

It is easily soluble in benzol, ether, chloroform, &c., hardly in alcohol.

(To be continued).

REDUCING AGENTS IN NORMAL HUMAN URINE.

By GEO. STILLINGFLEET JOHNSON.

My attention has been drawn to the following passage, which is a translation from the last edition of that well-known work "Analyse des Harns," by Neubauer and Vogel, v. p. 57 :—

"According to St. Johnson one should be able to remove all reducing substances, except sugar, from the urine as mercuric oxide compounds. The urine is treated with 1-20th of its volume of cold saturated solution of sodium acetate, and 1/4th of its volume of cold saturated solution of mercuric chloride; and after forty-eight hours the precipitate containing the uric acid and the kreatinin is filtered off. One removes the excess of mercury from the filtrate with H₂S, and this by boiling. But according to my experience the liquid then reduces better (schöner) than before."

The above passage is taken from the analytical part of the work, which is edited by H. Huppert, Prof. der Med. Chemie an der Universität zu Prag. I have carefully perused my publications on reducing agents in urine, and especially my paper on "Kreatinins" in the *Proc. Roy. Soc.*, vol. xliii., pp. 493—534, but I fail to find any passage in which I state that all reducing agents are removed from the urine by precipitation with mercuric chloride; on the contrary, the paper might be entitled "On the Substances in Urine which Resemble Sugar in Reducing Cupric Oxide in Boiling Alkaline Solutions."

Again, I have sought in vain for any passage in which I have directed that the excess of mercury should be removed from the urine by H₂S, filtering, and boiling.

Since my attention has been directed to the matter, I have employed the H₂S method for removing the excess of mercury, and I am able fully to confirm H. Huppert's statement that the liquid reduces better than the original urine, a fact which to my mind conveys the strongest evidence that the method employed has produced chemical changes in the dissolved urinary solids. I hope, therefore, that before consigning me and my works to oblivion, chemists may pause a moment and consider the following facts :—Some normal human urine was completely precipitated by sodium acetate and mercuric chloride. The filtrate was saturated with H₂S, filtered, excess of H₂S removed by evaporation in vacuo over solid KOH. The liquid reduced Fehling's solution on boiling.

The cupric-oxide reduction of a normal urine was estimated by Pavy's ammonio-cupric process, as equivalent to 0.1 gm. of glucose in 4.2 c.c. Some of the same urine was saturated with H₂S, the excess of H₂S removed by boiling, the liquid filtered, and made up to its original volume with the wash-waters. When subjected to the ammonio-cupric process, this liquid gave reduction equivalent to 0.1 gm. of glucose per 3 c.c.

Clearly, therefore, sulphuretted hydrogen gas forms in urine fixed reducing agents, which cannot be removed either by boiling or by evaporation in vacuo.

It only remains for me to describe the method which I myself employ for removing excess of mercury from the urine. I prefer simply to add ammonia water cautiously to the liquid as long as any precipitate forms. Not only

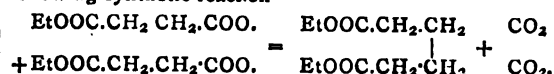
is the filtrate free from cupric oxide reducing action, but the precipitate also, after being washed and decomposed by H₂S under water, yields a filtrate which possesses no reducing action whatever.

King's College, London,
August 9, 1892.

ELECTROLYTIC SYNTHESIS OF DIBASIC ORGANIC ACIDS.*

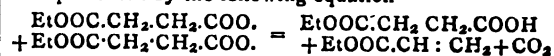
By Prof. CRUM BROWN and Dr. JAMES WALKER.

WHEN potassium ethyl malonate is electrolysed in strong aqueous solution, there occurs at the positive electrode, besides actions resulting in the evolution of oxygen, the following synthetic reaction—



Thus from malonic acid there is obtained succinic acid, the next member in the series of saturated dibasic acids. In the same way there may be obtained from succinic acid adipic acid; from adipic, sebacic; from glutaric, suberic; and from suberic and sebacic acids two new acids of the formulæ $\text{HOOC} \cdot (\text{CH}_2)_{12} \cdot \text{COOH}$ and $\text{HOOC} \cdot (\text{CH}_2)_{16} \cdot \text{COOH}$. Acids with side chains behave in a similar manner; thus from methylmalonic acid there are obtained the two inactive symmetrical dimethylsuccinic acids.

Amongst the other products of the electrolysis there are found ethyl ethers of unsaturated acids; for instance, acrylic ether in the case of the electrolysis of ethyl potassium succinate. The formation of this substance may be represented by the following equation—



The positive pole employed was a spiral of platinum wire, and the negative pole and platinum crucible of about 40 c.c. capacity. The E.M.F. was 12 volts, the current being about 4 to 5 amperes.

ON THE APPLICATION OF A HYDROGEN FLAME IN AN ORDINARY SAFETY LAMP TO THE DETECTION AND MEASUREMENT OF INFLAMMABLE GAS OR VAPOUR.*

By Prof. FRANK CLOWES, D.Sc.,
University College, Nottingham.

THE appearance of a "cap" over the flame in the safety-lamp has long been used by the coal miner for detecting "firedamp" in the air, and for roughly measuring its amount. The ordinary oil-flame does not with certainty detect the presence of less than 3 per cent of firedamp. The alcohol flame adopted by Pieler detects 0.25 per cent readily; but since this flame gives no light the Pieler lamp can be used for gas-testing only, and is useless for lighting purposes. At the last meeting of the British Association the results of an examination of the Ashworth lamp were given by the author; this lamp burns benzoline, and was found to give good illumination when the wick was raised, and to detect at least 0.5 per cent of firedamp when the wick was pulled down until it gave a pale blue flame only.

In the present paper the author describes a miner's safety-lamp, in which the ordinary flame can at once be replaced by a hydrogen flame when desired. The use of

* Read before the British Association, Edinburgh Meeting, 1892, Section B

the hydrogen flame enables the miner to detect readily and with certainty percentages of firedamp, varying between 0.25 and 3%, and to measure their amount. As soon as the delicate testing is finished the ordinary flame of the lamp is kindled, and can be employed either for illumination, or, if lowered, it can be applied to the detection of percentages of gas larger in amount than those found by the hydrogen flame. The hydrogen gas is carried in a small steel reservoir, slung over the shoulder by a strap, and is introduced through a fine metal tube which passes into the interior of the safety-lamp and terminates near the wick. This composite lamp is at once a good illuminator and an extremely delicate gas tester.

Comparative experiments were made with a hydrogen flame, an alcohol flame of the same height, and a small blue benzoline flame, all of which were exposed in air containing 1 per cent of coal-gas. The "cap" seen over the hydrogen flame was nearly four times as high as that seen over the benzoline flame, and half as high again as that seen over the alcohol flame.

Many serious accidents have arisen from bringing a "naked flame" into spaces in which light petroleum oil has been stored. The vapour of this oil, when mingled with the air in proper proportions, is violently explosive; and it becomes important therefore to have means of detecting its presence and measuring its amount. The author described tests carried out with the above hydrogen safety-lamp in his test chamber. They prove that the hydrogen flame can detect one-twentieth of the amount of petroleum vapour which can be kindled in air, and one thirty-sixth of the amount which explodes when mingled with air.

Mr. Vernon Harcourt, Mr. Thomas, of Cardiff, and Profs. Barrett and Smithells, took part in the discussion of the paper, and elicited the following further facts from the author of the paper. The proportion of inflammable gas in air is measured not only by taking the height of the cap but also by noting its appearance, which changes considerably as the percentage of "gas" rises. Further, that the size of the cap produced by a given percentage of gas is increased by the increased temperature and size of the flame. Since air containing less than 1 per cent of this gas is explosive if mixed with coal-dust, it becomes necessary to have a delicate test for gas to ensure the safety of dust mines.

THE EXPLOSION OF ETHYLENE WITH LESS THAN ITS OWN VOLUME OF OXYGEN.*

By B. LEAN, B.A., B.Sc., Dalton Chemical Scholar of
Owen's College, and
W. A. BONE, B.Sc., Fellow of Victoria University.

Our investigation arose out of experiments to determine the rate of explosion of hydrocarbons with defect of oxygen, and were made at the suggestion of Professor H. B. Dixon. We found that on exploding ethylene with less than its own volume of oxygen, there was invariably a considerable increase in pressure. In case of a mixture of 100 volumes ethylene to 96.5 volumes oxygen, the pressure increased from 756 m.m. to 1503 m.m. of mercury, indicating that the oxygen had mainly gone to the carbon and not to the hydrogen. On carefully analysing the products of explosion we found that, in addition to hydrogen, carbon monoxide, and small percentages of carbonic acid and unsaturated hydrocarbons, there was always present a small amount of some saturated hydrocarbon, presumably marsh gas.

We made and fired five different mixtures of ethylene and oxygen, containing 100 volumes ethylene to from 70 to 96.5 volumes oxygen. We invariably found both

* Read before the British Association, Edinburgh Meeting, 1892, Section B.

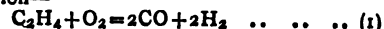
saturated and unsaturated hydrocarbons present in the products of the explosion, and the percentages of both these increased as the percentage of oxygen in the original mixture decreased, as one would naturally expect.

The quantity of marsh gas present in the products of explosion of 100 volumes of ethylene to 70 volumes of oxygen was 5.53 per cent, and in the case of the mixture containing 100 volumes ethylene to 96.5 volumes of oxygen, we found 1.01 per cent of marsh gas in the products.

With regard to the unsaturated hydrocarbons present in the products, a qualitative examination revealed the presence of acetylene. Whether this constitutes the whole of the unsaturated hydrocarbons present we are not prepared to say; it is certainly present in not inconsiderable quantities.

We may be allowed to add a note as to the nature of the reaction when ethylene is exploded with less than its own volume of oxygen.

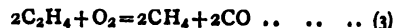
The first reaction which doubtless occurs is a combination between the oxygen and part of the ethylene with the formation of carbon monoxide and hydrogen, according to the equation—



The heat liberated by this reaction produces a decomposition of some of the unburnt ethylene analogous to the decomposition which ethylene undergoes when passed through a red-hot tube into marsh gas and carbon, according to the equation—



Marsh gas might also be produced in another way, by partial oxidation and decomposition, according to the equation—



With regard to the formation of acetylene, this is most probably due to a secondary reaction between the nascent hydrogen formed according to equation (1), and the deposited carbon according to equation (2)—



The value of our experiments lies largely in the fact that as a result of the extremely short period during which the reaction lasts in the explosion coil, the gaseous products must be, in the main, those produced by the original primary reaction, for the rapid cooling of the gases retards the progress of any complicating secondary reaction.

Our investigations have an important bearing upon the question of the luminosity of hydrocarbon flames. The view that the separated carbon, which doubtless is a cause of luminosity, is due to the fact that oxygen combines with hydrogen in preference to carbon can no longer be held. Our work shows that oxygen combines with the carbon in preference to the hydrogen; and in the case of an ethylene flame separated carbon is probably due to the decomposition of ethylene into marsh gas and carbon at high temperatures.

In conclusion we beg to thank Prof. Dixon for many valuable suggestions and kindly oversight of our work.

ATOMIC WEIGHT OF BORON.*

By W. RAMSAY, Ph.D., F.R.S., and EMILY ASTON,
B.Sc. (Lond.).

We have made a re-determination of the atomic weight of boron by the following methods:—

1. A preliminary re-determination of the water of crystallisation in borax.

2. Conversion of anhydrous sodium borate into sodium chloride by distillation of the borax with hydrochloric acid and methyl alcohol, and weighing the resulting sodium chloride.

* Read before the British Association, Edinburgh Meeting, 1892, Section B.

TABLE I.

Expt. No.	Weight of crystalline borax.	Weight of fused borax.	Percentage of water lost.	Atomic weight of boron.
3	10'3581602	5'4784357	47'1099	11'04
5	5'3440080	2'8246677	47'1433	10'97
6	4'9962580	2'6378934	47'2026	10'85
7	5'7000256	3'0101127	47'1912	10'87
9	5'3142725	2'8065646	47'1882	10'88
11	4'9971924	2'6392016	47'1865	10'885
12	5'2360921	2'7674672	47'1524	10'955
Aggregate ..	41'9466088	22'1631808	47'1633	10'93

Mean atomic weight B = 10'921.

Probable error $\pm 0'010$.

TABLE II.

Expt. No.	Weight of fused borax.	Weight of sodium chloride.	Atomic weight of boron.
14	4'7684431	2'7597665	11'015
15	5'2740315	3'0578213	10'925
16	3'2344088	1'8727203	10'992
17	4'0861923	2'3713122	10'879
18	3'4970297	2'0265645	10'949
Aggregate ..	20'8601057	12'0881848	10'951

Mean atomic weight B = 10'952.

Probable error $\pm 0'010$.

TABLE III.

Expt. No.	Weight of fused borax $\text{Na}_2\text{B}_4\text{O}_7$.	Weight of sodium chloride NaCl.	Atomic weight of boron.	Weight of silver chloride AgCl.	Chlorine p.c. in sodium chloride.	Atomic weight of boron from chlorine.
22	5'3118075	3'0761181	10'983	7'525869	60'493	11'071
23	4'7805583	2'7790458	10'955	6'7794186	60'515	11'024
24	4'9907395	2'8929844	10'936	7'0804317	60'516	11'003
25	4'7231225	2'7360411	10'968	6'6960242	60'514	11'039
26	3'3137921	1'9187258	10'972	4'6931271	60'479	11'091
Aggregate ..	23'1200199	13'3939152	10'965	32'7748706	60'505	11'084

Mean atomic weight of boron 10'966.

Probable error $\pm 0'005$.

Mean atomic weight of boron 11'052.

Probable error $\pm 0'010$.

Pure borax was prepared from pure boracic acid and pure soda. It was found to be an efflorescent substance, so the estimation of the water of crystallisation is hardly a method suited for an atomic weight determination. We made our experiments upon it during damp weather, so that the loss of water that it underwent was not great.

Method I.

Determination of the water of crystallisation in borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

A weighed quantity of borax, generally about 5 grms., was placed in a platinum dish, and heated in an air-bath at a temperature of about 90° – 110° C. for some time; the temperature was gradually raised to about 350° C.; the borax swelled up very much, and in some cases there was loss by spurting; the dish was then taken out of the air-bath, and the borax fused over the blow-pipe; it was then allowed to cool in a desiccator, and the fused borax weighed. The loss in weight gave the percentage of water, from which the atomic weight was calculated.

The results are given in Table I. The mean atomic weight obtained is 10'921 for boron.

The atomic weights used in the calculations are:— $\text{H} = 1'008$; $\text{O} = 16$; $\text{Na} = 23'05$; $\text{Cl} = 35'45$; $\text{Ag} = 107'92$.

Method II.

Distillation with methyl alcohol and hydrochloric acid.

A weighed quantity of anhydrous borax was dissolved in a small quantity of water, alcohol added, and an excess of pure hydrochloric acid; it was then distilled on a water-bath with addition of methyl alcohol, till boracic acid could no longer be detected in the distillate by the flame test. The flask was then dried in an air-bath at a temperature of about 100° – 110° C. in a slow current of air. The temperature was then raised to about 350° for two or three hours to drive off the last traces of water; the flask was then left to cool, and weighed after it had stood for some time in the balance case.

The weight of salt obtained from the borax was thus determined; the sodium present was calculated; from this number the amount of borax corresponding to two atomic proportions of sodium was found; this number, less Na_2O , gave B_4 , and hence the atomic weight of boron.

In the first series of experiments a flask of soft glass was used. The results obtained were not very concordant, for the glass was attacked, replacement of oxygen by chlorine took place, resulting in the formation of silica and sodium chloride from sodium silicate, for on dissolving the salt in water an insoluble residue of silica was left.

The results are given in Table II.; the mean atomic weight is 10'952, and is not far from that obtained in the next series of distillations.

Second Series.

To avoid the error introduced by the action of the hydrochloric acid and alcohol upon the soft glass, a flask made of combustion tubing was used. It was found that this glass was hardly acted upon, but when the salt was dissolved in water a very slight residue of silica was left. In order to check the results, the chlorine in the sodium chloride was estimated with silver nitrate in the usual manner; the silver chloride was collected on a Gooch's filter, and dried in an air-bath at a temperature of about 200° C. The results obtained gave a rather low percentage of chlorine; calculated with Clarke's atomic weights it is 60'598. If the atomic weight of boron is determined from the chlorine, it is rather higher than that given from the weight of salt.

Since no special precautions were taken to obtain pure silver for the chlorine determinations, but ordinary silver nitrate was employed, it is probable that the distillation results yield the more correct atomic weight of boron, which is therefore 10'966.

METHODS OF SUGAR ANALYSIS.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION
OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

(Concluded from p. 73).

PLAN B.—Official Instructions for the Examination of
Chocolates, Candies, and Liquors for the Quantity of
Sucrose contained therein.

A.—THE examination, especially of chocolates, preserved fruits, and liquors, must be primarily directed toward the detection of starch sugar or honey.

B.—The Soleil-Ventzke saccharimeter is used in the sucrose determinations. The directions for the use of the instrument will be found in Plan C of the Official Bulletin published as an appendix to the sugar tariff law of July 9, 1887.

Ventzke's scale is so arranged that a 200 m.m. tube filled with a sugar solution containing 26.048 grms. per 100 c.c. will read 100.

If 26.048 grms. of a substance are weighed out, dissolved in 100 c.c. of water, and polarised in a 200 m.m. tube, the number of degrees read on the scale will be the per cent by weight of sugar in the material.

The same is the case when 13.024 grms. are dissolved in 50 c.c. If this weight (one-half normal weight) has been dissolved in 100 c.c. the reading of the polariscope must be doubled.

If any other quantity (p grms.) was weighed out, dissolved in 100 c.c., and polarised in the 200 m.m. tube, the number of degrees read on the scale (a) $\times$ 0.26048 will give the grms. sucrose in 100 c.c. of the solution, and—

$$\frac{26.048 a}{p}$$

will give the per cent sucrose in the substance analysed.

In all cases where the substance to be examined contains no other optically active bodies, the direct polarisation will give accurate results. If such are present, as, for instance, glucose, invert sugar, maltose, dextrin, pectinous bodies, the application of the polariscope becomes uncertain, and only in a few cases, which will be given below, can somewhat reliable results be obtained.

As regards the preparation of the solutions the following must be remembered:—Material which consists mostly of sucrose and leaves only a small residue on being treated with water, can be weighed out in the dish, and the solution immediately transferred to the sugar flask. When the substance, however, contains much insoluble matter, the latter should not be washed into the flask, as the volume of the sugar solution in such a case would be less than 100 c.c. In this case the residue must be separated from the solution by filtration and washing. Generally the sugar solution is not quite transparent, and must be treated with some clearing agent. The solutions serving this purpose are:—

1. Lead acetate, of which from 1 to 10 c.c. are mixed with the solution and the latter filtered after standing from fifteen to thirty minutes.
2. Lead acetate with subsequent addition of alum or aluminum sulphate, the lead sulphate formed carrying down the foreign matter.
3. Aluminum hydrate in the form of a thin paste, of which several c.c. are shaken with the solution.
4. Tannic acid, to precipitate albuminous substances. This must be examined beforehand with regard to its optical activity.
5. Charred blood or bone-black, to remove colouring-matter, $\frac{1}{2}$ to 1 grm., are added to the liquid.

In some cases this clearing is difficult, and the method best adapted must be determined by previous experiments. For solutions prepared from candies the pasty aluminum hydrate is the best medium.

When, as is often the case, invert sugar is present, the result of the direct polarisation will be too low on account

of the left handed rotation of this sugar. In such a case, Clerget's inversion method must be applied to find the correct per cent of sucrose. This is conducted as follows:—26.048 grms. are dissolved in a sugar flask and the solution made up to 100 c.c.; 50 c.c. of this solution are transferred by means of a pipette to a 50 or 55 c.c. flask, cleared, and polarised, the reading being corrected for the extra 5 c.c. The liquid adhering to the pipette is washed into the 100 c.c. flask containing the remaining 50 c.c. (13.024 grms.), 5 c.c. of concentrated hydrochloric acid (38 per cent, specific gravity 1.88 at 15° C.) added, and the flask heated for fifteen minutes at 67° to 70° C. in a water bath. The temperature should not exceed this limit. The flask is then cooled rapidly and the solution made up to 100 c.c. If the liquid is coloured, it is shaken with $\frac{1}{2}$ to 1 grm. of bone-black, and filtered through a double filter. It is then polarised in a 200 m.m. tube, which is provided with a thermometer. As the rotatory power of invert sugar is much influenced by the temperature, this factor must be regarded. The reading is best taken between 18 and 22° C., and the temperature accurately determined. The reading must also be doubled on account of the dilution of the liquid.

To calculate per cent of sucrose (R) the two readings are added together, the sum (S) multiplied by 100 and divided by $142.4 - \frac{1}{2}t$; where t is the temperature at which the invert reading was taken. If the temperature is exactly 20° C., the result can be made more accurate by substituting 142.66 for 142.4, thus:—

$$R = \frac{100 S}{142.66 - \frac{1}{2}t} = \frac{100 S}{132.66} = 0.7538 S.$$

If very much invert sugar is present, both the direct and indirect readings must be taken at the same temperature.

I.—Chocolate.

Weigh out in a German silver dish 13.024 grms. of the rasped chocolate, moisten with alcohol (to aid the solution in water), add 30 c.c. of water, and heat for ten to fifteen minutes on the water bath. Filter while warm into a 100 to 110 c.c. flask, using a folded filter, any turbidity of the filtrate not being of any consequence. The residue on the filter is washed with hot water until the filtrate amounts to about 100 c.c. Five c.c. of lead acetate are then added, the liquid allowed to stand fifteen minutes, and a few drops of alum solution and some moist aluminum hydrate added. The liquid is then made up to 110 c.c., shaken well, and filtered through a folded filter. Slight moistening of the filter will aid filtration, but the first 25 c.c. of filtrate should then be rejected. The polarisation should be increased by one-tenth and then doubled.

II.—Candies and Confectionery.

(a) *Dragees* (seeds or kernels coated with sugar and flour).—26.048 grms. are covered in a beaker with 40 to 50 c.c. of water and allowed to stand, stirring now and then, until the mass is completely saturated. If the liquid shows an acid reaction, some precipitated calcium carbonate or a few drops of ammonia are added. The larger particles are now separated by filtering through cloth, the filtrate being collected in a 100 to 110 c.c. flask. The residue on the filter is washed with cold water until about 100 c.c. of the filtrate have accumulated. Some aluminum hydrate is then added to clear it, the solution made up to 110 c.c. with water, and about half a grm. of bone-black added in case the liquid is coloured. It is then allowed to stand half an hour, with occasional shaking. The solution is finally filtered through a dry folded filter.

A preliminary test for invert sugar is made with copper sulphate and soda-lye, and the solution analysed accordingly. Dragees almost always contain invert sugar.

(b) *Raffinade Wafers* (cane sugar, with ethereal oils and colouring matter).—26.048 grms. dissolved in water, made up to 100 c.c. in flask, and, if necessary, de-

coloured with bone-black. A preliminary test for invert sugar must always be made and the analysis directed accordingly.

(c) *Santonin Wafers* (worm wafers, cane sugar, with santonin and some agglutinant, as egg albumen).—13.024 grms. dissolved in a 100 c.c. flask (the santonin being insoluble), 5 c.c. of lead acetate added, with a few drops of alum solution, the solution allowed to stand some time, with occasional shaking, made up to 100 c.c. and filtered.

(d) *Dessert Bonbons* (Fondant's, Praline's, chocolate bonbons, consisting of cane sugar or invert sugar, serving as a covering for marmalade, fruit, or chocolate).—13.024 grms. are treated with water and a few drops of ammonium hydrate until dissolved. If only a slight residue remains the whole can be immediately transferred to a 100 c.c. flask, otherwise it must first be filtered. One-half of the liquid is inverted, the other polarised directly after having been cleared by means of aluminum hydrate in a 50 to 55 c.c. flask.

(e) *Marsipan Masse* (cane sugar, with crushed almonds).—13.024 grms. material are triturated in a porcelain mortar with cold water, then mixed in a flask with 50 c.c. of water and about 30 c.c. of pasty aluminum hydrate, well shaken, and filtered into a 200 c.c. flask. The residue on the filter is washed with water until the filtrate amounts to 200 c.c. As this candy contains no invert sugar, the solution can be polarised directly in the 200 m.m. tube, the reading being multiplied by 4 to correct for the dilution.

(f) *Cakes and Sweetened Pastry*.—26.048 grms. of the powdered material are mixed in a flask with about 75 c.c. alcohol (85 to 90 per cent) and allowed to stand one half hour in a warm place. It is then filtered through a fine cloth filter and the residue washed several times with alcohol. The filtrate is collected in a porcelain dish and heated on the water-bath until the alcohol has all been driven off. One half gm. bone-black is then added and the solution filtered into a 100 c.c. flask. 50 c.c. are used for inversion, the remained polarised directly.

(g) *Sugar-Coated and Preserved Fruits* (marmalade, compots, jellies).—A considerable amount of invert sugar and pectinous bodies are always present. The aqueous solution of the latter has no rotatory power. If the material is solid in consistence, a crushed or finely-cut average sample must be prepared. 13.024 grms. are then mixed with 30 to 50 c.c. of water and a few drops of ammonium hydrate (to neutralise any free vegetable acids), and allowed to stand several hours. It is then passed through a cloth filter into a 100 or 200 c.c. flask, the residue washed several times with hot water, and about 10 c.c. of aluminum hydrate and one half gm. bone-black added to the filtrate. It is then shaken and made up to the mark. After filtering the filtrate is polarised according to Clerget's method.

Fruit jellies and marmalade are analysed in a similar manner.

If the sucrose articles enumerated under II., g, was calculated by the formula—

$$R = \frac{100 S}{142.4 - \frac{1}{2} t},$$

we would only obtain the percentage present at the time of analysis. The acids of the fruit have, however, converted a large amount of the cane sugar originally used into invert sugar. The original percentage of cane sugar, which is taken as a basis for taxation by the Custom-house, can be calculated from the reading of the inverted solution. If this reading is referred to 26.048 grms. material dissolved in 100 c.c. and polarised in a 200 m.m. tube, we have the following relations if the above figure is called B:—

A solution of 26.048 grms. of cane sugar in 100 c.c. has, after inversion, at the temperature t° the left handed

rotation $42.4 - \frac{1}{2} t$. The amount of cane sugar corresponding to the observed polarisation B can thus be calculated by the proportion—

$$42.4 - \frac{1}{2} t : 26.048 = B : \frac{26.048 \cdot B}{42.4 - \frac{1}{2} t},$$

and this is contained in 26.048 grms. of the material used. Therefore the original percentage r of cane sugar can be calculated from the second proportion.

$$26.048 : \frac{26.048 \cdot B}{42.4 - \frac{1}{2} t} = 100 : r$$

whence—

$$r = \frac{100 B}{42.4 - \frac{1}{2} t}$$

If 13.024 grms. substance were used and the solutions polarised at exactly 20°C ., then the following formula is more accurate:—

$$r = \frac{100 B}{42.66 - 10} = 3.062 B.$$

III.—Liquors.

The percentage of sugar in liquors is generally expressed as grms. per litre.

Every liquor must be previously tested for invert sugar by diluting a little in a test-tube with water, adding five drops of copper sulphate solution and enough sodium hydrate to form a clear blue liquid. If no change occurs upon heating, cane sugar only is present; a yellow or red precipitate indicates the presence of other sugars.

Liquors which do not contain invert sugar may be polarised directly in the 200 m.m. tube, being previously decolourised with bone-black if necessary. If a high percentage of sugar is present, the polarisation must be made in the 100 m.m. tube.

The presence of alcohol has no influence on the reading. The ethereal oils which are present, although optically active, are present in such small quantities as to be without influence. The grms. per litre (R) are found, when A is the reading in a 200 m.m. tube, by: $R = 2.6048 A$.

When invert sugar is present the alcohol must be removed, as it materially changes the rotation of this sugar.

Fifty c.c. of liquor are measured into a porcelain dish and evaporated to about one-half the volume on a water-bath. If the liquid has an acid reaction, a few drops of ammonium hydrate must be added before heating it. The residue is washed into a 100 c.c. flask and made up to the mark with water. One-half is then polarised directly, the other after inversion. Both solutions may have to be decolourised with bone-black.

Supposing—

V = number of c.c. used for analysis,

A = direct reading,

B = reading of inverted solution (both read in 200 m.m. tube),

t = temperature of inverted solution when polarised,

then the grms. of cane sugar (R) in a litre may be calculated from the formula—

$$R = \frac{26.048 (A - B)}{(142.4 - \frac{1}{2} t) V},$$

where, when the direct reading was +, the inverted reading —, the difference $A - B$ becomes $A + B$.

If the temperature was exactly 20°C .,—

$$R = 196.7 \frac{A + B}{V}, \text{ or more accurately } = 196.35 \frac{A + B}{V},$$

In liquors, as under III., b, the addition of the fruit juices may have caused inversion of a part of the cane sugar originally added. The original percentage of cane

sugar is then calculated from the inverted reading just as for candied fruits. The grms. of cane sugar (r) per litre are found from—

$$r = \frac{26.048 B}{(42.4 - \frac{1}{2} t) \bar{V}},$$

or when $t = 20^\circ$,—

$$r = 804 \frac{B}{\bar{V}}, \text{ or more accurately } = \frac{26.048 B}{32.66 \bar{V}} = 797.55 \frac{B}{\bar{V}}.$$

PLAN C.—Directions for Determining the Bonificatus Value of Invert Sugar Syrup.

While the syrup is being barrelled, a number of samples are taken so as to obtain a good average. This is well mixed and 250 grms. weighed out in a tared beaker. After dissolving in distilled water, the beaker is placed on the balance and enough water added to bring the weight of syrup and water up to 1000 grms. The syrup has then been diluted with three times its weight of water. The solution is again well mixed with a glass rod and poured into a high cylinder. A special spindle is used to determine the percentage of invert sugar. This spindle is used similarly to the Brix spindle for analysing syrups. It is graduated at 174°C. , and the following table is used to correct for the temperature:—

Subtract from the reading.		Add to the reading.		Add to the reading.	
At 10°C.	Brix. 0.35°	At 18°C.	Brix. 0.03°	At 25°C.	Brix. 0.50°
11°C.	0.29°	19°C.	0.09°	26°C.	0.57°
12°C.	0.25°	20°C.	0.17°	27°C.	0.64°
13°C.	0.22°	21°C.	0.24°	28°C.	0.71°
14°C.	0.18°	22°C.	0.31°	29°C.	0.79°
15°C.	0.14°	23°C.	0.38°	30°C.	0.87°
16°C.	0.10°	24°C.	0.44°		
17°C.	0.04°				

The reading is multiplied by 4 to obtain the per cent of invert sugar in the undiluted syrup. Hundredths are always read as an additional tenth.

Example.—The spindle read 18.1 per cent invert sugar at 20° . Hence 0.17° must be added to the reading and the sum multiplied by 4.

$$18.1 + 0.17 = 18.27 \times 4 = 73.08, \text{ or } 73.10.$$

The weight of the cane sugar used in the preparation of the syrup is then calculated by subtracting 1.20th, and multiplying the result by the weight of the invert sugar syrup.

NOTICES OF BOOKS.

Chemistry of the Organic Dye-Stuffs. By R. NIETZKI, Ph.D., Professor at the University of Basle. Translated, with additions, by A. COLLIN, Ph.D., and W. RICHARDSON. London: Gurney and Jackson (successors to Mr. Van Voort).

THE value of Professor Nietzki's work has been widely recognised in Germany, and the translators merit the gratitude of all persons connected with the tinctorial industries for having executed the present version.

The author begins with a useful introduction, in which he explains the nature of chromophors, chromogens, and auxochromes. The respective theories of dyeing, the chemical and the mechanical, are stated, but no final conclusion is reached. The statement that vegetable fibres, in contradistinction to animal fibres, "require the intervention of a special mordant," though generally true is too sweeping. Carthamine we all know is readily taken up by cotton.

For determining the commercial value of a colouring-

matter, the author pronounces trial dyeings the only trustworthy method. This conclusion, in as far as it is well founded, is to be regretted. The working dyer, from prejudice or from more questionable motives, sometimes declares dye-ware supplied by some particular firm or firms inferior in quality. Hence processes of a different nature are exceedingly valuable for checking his assertions.

Prof. Nietzki divides the organic colouring-matters into fourteen groups, or rather into fifteen groups and a residue which so far refuses to be classified.

The reader when considering the vast number of coal-tar colours, actual or practical, must not suppose that all or even the majority of these are in practical use. Some, as it will be found in the work before us, have remained mere laboratory curiosities, others have been used for a time and then discarded as too fugitive, too costly, too difficult of application, or very often merely as possessing no distinctive advantages over others already in use.

Berberine is a curious instance of a natural dye-ware having basic properties capable of being fixed on the fibre like the basic aniline dyes. It is found naturally in calumba and barberry roots and belongs to the quinoline group of dyes.

In Chapter XV. the author considers the dye-ware of unknown constitution, most of which are natural products. Many of these, the author admits, are indispensable in dyeing, since no synthetical products have been able to do their work.

Against the use of bixin—in the form of annatto—for colouring butter and cheese we have protested elsewhere, on account of the loathsome manner in which it is often prepared. Bixin, in the crude material, is accompanied by another dye-ware, orelline, the composition of which has not yet been determined.

Curcumine, the colouring principle of turmeric, is still extensively used. Unlike the majority of dyes, it is fixed upon cotton without the intervention of a mordant, though not very firmly. Mordants, indeed, by no means improve the turmeric shades either in fastness or brilliance.

It is unfortunate that all the attempts made to reduce the yellow colouring-matter of safflower into carthamine have so far failed.

Cochineal and also lac-dye have found their most dangerous rival in the scarlet-red azo-compounds.

In the present work it is pointed out that the colouring principle of lac-dye, laccainic acid, $\text{C}_{16}\text{H}_{12}\text{O}_8$, is distinct from that of cochineal.

The name Tyrian purple, here rightly applied to the colouring-matter of certain mollusca (*Purpura lapillus*, *P. hamastoma*, and *Murex* sp.), was unfortunately at one time applied to murexide. The confusion is of the less importance as a sufficient supply of uric acid for the production of murexide on the large scale was not available.

The so-called "patent colours" of Croissant and Bretonnière figure here under their French name of Cachon de Laval. Their very unpleasant smell, here noticed, is much complained of by many dyers.

Throughout this work the author deals "only with the general principles involved in the manufacture of individual dye-ware, as details for their technical production are untrustworthy, owing to the continuous developments taking place in the industry in question." On this fact there might be founded a very serious argument against granting patents for chemical inventions. Too many chemical patentees use their specification not as an ultimatum by which they are prepared to stand or fall, but as a screen behind which they can indulge in additions, omissions, or modifications.

For technical details, the author refers to Hummel's work. We hope that the joint undertaking of Professor Nietzki, Dr. Collin, and Mr. Richardson will prove signally successful.

CORRESPONDENCE.

A CURIOUS POINT IN THE HISTORY OF
THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—There is a very curious omission in the volume of the *Journal of the Chemical Society* for the year 1868. The Anniversary Meeting held March 30, 1868, is reported in the volume. The report begins on page 1, the first mention being that Mr. Warren de la Rue, F.R.S., President, in the Chair, read his report (which follows); then there is the balance sheet on page 36, but there is no mention whatever of the election of "officers and council for the ensuing year."

The question has arisen, "Did the Society elect officers and council for the period between March 30, 1868, and 1869?" Nowhere in the volume for the year 1868 is there the list of officers and members of the council.

As any Fellow of the Society who possesses early volumes of the journal may ascertain for himself, the custom used to be to publish the list of officers and council immediately after the address of the President. Why was that custom departed from in the year 1868? At that time I was a Fellow of the Society, and indeed from March, 1867, to March, 1868, I served as a member of the council. Whether I was in office or not from March, 1868, to March, 1869, I do not know; and there is (as I have said) nothing in print in the volumes of the journal which throws any light on the subject. There is a curious interest attached to this strange irregularity.—I am, &c.,

J. ALFRED WANKLYN.

ESTIMATION OF CAOUTCHOUC.

To the Editor of the Chemical News.

SIR,—Referring to the analysis of rubber by Mr. H. J. Phillips, published in the *CHEMICAL NEWS* for August 5, I note that caoutchouc is given as 54.26 per cent. It most probably is as much as that, but a considerable quantity, if not almost all, of this caoutchouc is old rubber worked up again, and has a very different effect to pure rubber.—I am, &c.,

J. K. BURBRIDGE.

Tottenham, August 15, 1892.

WANTED,—CONSISTENCY.

To the Editor of the Chemical News.

SIR,—I am under the impression that oft-times I have noticed in your columns a sad remonstrance with the authors of text books,—which you have been compelled to pass in the second class, albeit they aspire to pass others in the first class,—called forth by the use of the suffix *ic*, where it was in your opinion unnecessary and even misleading to the crammee.

It would be interesting, therefore, to hear on what grounds such an undoubted authority as the President of the Chemical Section of the British Association for the Advancement of Science employs the said suffix so glibly, and in an address which is itself somewhat of an appeal for consistency. Doubtless he has prepared magnesium sulphate and sodious chloride. I for one am on the tip-toe of expectation.—I am, &c.,

Ous.

Determination of the Specific Gravity of Sparingly Fluid Substances.—J. W. Bruehl (*Ber. Deutsch. Chem. Gesell.*).—The author has devised a pyknometer with a neck wider than usual and with a lateral tube, to which a water air-pump can be attached.

CHEMICAL NOTICES FROM FOREIGN
SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

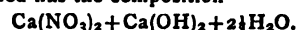
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 3, July 18, 1892.

Preparation and Properties of Carbon Diodide.—Henri Moissan.—To prepare this compound the pure tetraiodide of carbon is introduced into a very dry flask with a quantity of tetrachloride or of disulphide sufficient for its solution. It is refrigerated in a current of water, and the quantity of silver powder necessary to remove half the iodine is introduced in small portions. The flask is then sealed up, and the reaction is allowed to proceed in the cold until the liquid has merely a pale yellow colour. The protoiodide, C_2I_4 , forms fine crystals of a bright yellow colour, of specific gravity 4.38, fusible at 185° , and volatile without decomposition above their melting-point. It is very soluble in carbon disulphide, in the tetrachloride, and in ordinary ether, which, on cooling, deposits it in fine crystals. It is sparingly soluble in cold, anhydrous alcohol, but dissolves on boiling. It does not react with hydrogen; chlorine and iodine do not attack it in the cold, but in heat they form a bromiodide and a chloriodide. If heated in oxygen the protoiodide melts, and is then dissociated into iodine and carbon. At 110° it is not attacked by sulphur, but at higher temperatures iodine is eliminated and carbon disulphide is formed. It is not oxidised by boiling monohydrated nitric acid, by chromic acid, or by dilute solutions of permanganate.

One of the Reactions of Spermine.—M. Duclaux.—The author shows that the alleged oxidising property of spermine is not special, but is common to all bodies which render water viscid or frothy, soap-lye, saponine, panamine, &c.

Election of a Foreign Associate of the Academy.—Herr Van Beneden was elected *vice* Sir George Airy by thirty-five votes, Professor Nordenskiöld receiving only three votes and Dr. Lister two.

A Basic Calcium Nitrate.—A. Werner.—The compound obtained has the composition—



On heating this substance to 160° in a U-tube in a current of dry air, it loses its water of crystallisation and becomes—



Water immediately decomposes this salt. The existence of a basic salt formed by nitric acid combined with an alkaline substance like lime deserves attention as a mark of the kinship between the constitution of nitric acid and the phosphoric and arsenic acids.

The Efflorescence of Copper Sulphate and some other Metallic Sulphates.—H. Baubigny and E. Péchard.—The sulphates experimented on have been those of copper, cobalt, and zinc, beside the double sulphates of cobalt and potassium, zinc and potassium, ammonium alum, and chrome alum. According to the results of the authors in the simple sulphates studied, the rapidity of efflorescence may be considerably modified by the presence of small quantities of sulphuric acid in the liquid from which they have been crystallised. It will therefore be necessary when we wish to obtain stable hydrates for these sulphates to ascertain if their solution is perfectly neutral to methyl-orange.

The Decomposition of Basic Nitrates by Water.—G. Rousseau and G. Tite.—Last year the authors observed that copper subnitrate, if heated for some hours with water at from 150° to 160° , was entirely transformed into

copper oxide. They have since found that this decomposition has a certain generality. They have observed it in the basic nitrates of zinc, cadmium, and calcium, to which they now add bismuth and uranium.

The Phosphopalladic Compounds.—E. Fink.—M. Schützenberger has demonstrated the existence of a series of compounds containing platinum, phosphorus, and chlorine. The author has prepared similar compounds with palladium in place of platinum.

The Mechanical Contrast between the Radicle Cyanogen and the Halogenous Elements.—G. Hinrichs.—The author seeks to show that the monovalent radicle of cyanogen has not a composition of the same order as the simple and monovalent radicle of chlorine, or that it is impossible in mechanics to consider the elements as undecomposed radicles. In other words, the chemical elements, if they are complex substances, are not of the same order of composition as the common radicles.

Influence of the Methyl-Group, substituted for a Benzenic Hydrogen, upon the Properties of Orthotoluidine.—A. Rosenstiehl.—This paper will be inserted in full, if possible.

The Instability of Carboxyl in the Acid Phenols.—P. Cazeneuve.—The author finds that the instability of carboxyl united to a benzenic nucleus increases with the number of the phenolic hydroxyles which also occur in the molecule, and that the instability of the carboxyl seems to increase in the acid phenols with the substitutions—halogenous or other—in the nucleus. It is very probable that the general rule is that in the acid phenols the phenolic hydroxyles have a variable influence upon the stability of the carboxyl according to their position.

On Ferruginous Mineral Waters Preserved.—J. Riban.—The author maintains, very sensibly, that all discussion seems useless.

A New Leucomaine.—Dr. A. B. Griffiths.—The leucomaine in question, $C_{12}H_{16}N_2O_7$, is extracted from the urine of epileptic patients. It forms a crystalline hydrochlorate and chloraurate. With mercuric acid it gives a greenish white precipitate; with silver nitrate a yellowish precipitate, a white with phosphotungstic acid and a brownish white with phosphomolybdic acid, and a yellow with tannic acid. It is poisonous.

Journal für Praktische Chemie.
New Series, Vol. xlv., Parts 4, 5, and 6.

The Action of Alkalies upon the Iodalkylates of the Quinoline and Acridine Series.—Hermann Decker.—This bulky treatise does not admit of abstraction.

Nomenclature of Nitrogenous Nuclei.—O. Wiedman.—The author criticises the proposals of Knorr and of Hautsch.

Compounds of Chromammonium Sulphocyanide.—Odin T. Christensen.—A very full account of the reactions of Reinecke's salt (ammonium diamminochromosulphocyanide), $Cr_2NH_3(SCN)_3 \cdot NH_4SCN \cdot H_2O$.

Researches from the Laboratory of the University of Freiburg.—These consist of papers on γ -bromquinoline by Ad. Claus, and on the halogenalkylates of the oxyquinolines, and their decomposition by alkali and by silver oxide, by Ad. Claus and H. Howitz.

Contributions to the Chemistry of the Chromammonium Compounds; Chapter X. on the Rhodochrom Salts.—S. M. Jørgensen.

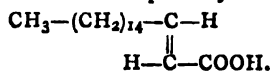
Constitution of the Cobalt, Chrome, and Rhodium Bases.—S. M. Jørgensen.—Both these memoirs, though very valuable, are unfit for abstraction.

A New Laboratory-Burner.—N. Teclu.—This paper requires the accompanying figure.

Analysis of the Julianen Brunnen and the Georgen Brunnen at the Eilsen Baths.—R. Fresenius.—Both these springs are very rich in sulphuretted hydrogen.

Experiments on the Preparation of New Organic Phosphorus Compounds.—Paul Heermann.—Although the author's researches do not definitely prove that phosphene or its derivatives, &c., are incapable of existence, they seem to show that the analogy of phosphorus and nitrogen here fails us and involves a decidedly different course of reaction, so that the compounds in question are produced either with difficulty or not at all.

Stereoisomerism of Oleic and Elaidic Acids.—Alex. Saytzeff.—Elaidic acid, like oleic acid, yields as its main product not oleic acid but an isomer, iso-oleic acid. Its stereochemical formula is probably—



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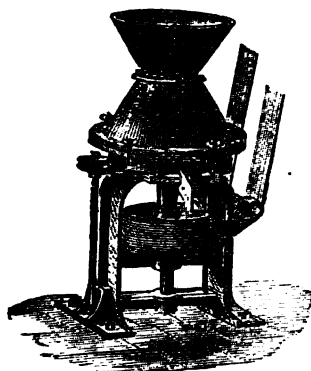
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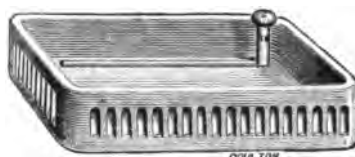
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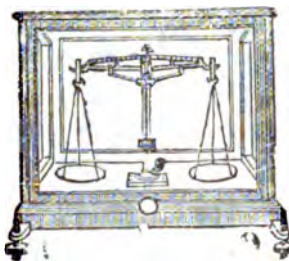
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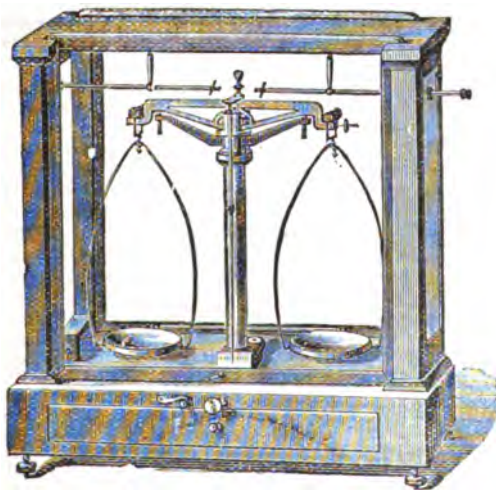


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THE CHEMICAL NEWS.

Vol. LXVI., No. 1709.

NOTE ON THE LUMINOSITY OF HYDROCARBON FLAMES.*

By VIVIAN B. LEWES,
Royal Naval College, Greenwich.

EVER since Sir Humphry Davy, in 1817, advanced his celebrated theory as to the causes of luminosity of certain flames, the subject has commanded a great amount of attention, and the researches of Berzelius, Waldie, Volger, Hilgard, Landolt, Frankland, Stein, Heumann, Kersten, and more recently those of Soret, Birch, Stokes, and Smithells, have all added to our knowledge of the subject, but even now many points remain to be cleared up before we can gain a clear conception of the numerous factors and interactions which go to make up a luminous flame, and it is in hopes of raising a discussion upon some of these points that I venture to bring this paper before you.

Certainly the two most important land-marks in the history of luminous flames are the original enunciation of the solid particle theory by Davy and Frankland's celebrated attack upon that theory in 1868. The relative values of the views of these two great experimentalists have been so recently discussed that it would be useless to again go through the mass of evidence which has accumulated during the past twenty-five years, and which seems to point conclusively to the luminous flame of burning hydrocarbons, owing their power of emitting light to the presence of incandescent particles of practically pure carbon; whilst, on the other hand, I believe I am correct in saying that Dr. Frankland is unshaken in his belief that the cause of luminosity is to be found, not in solid particles of carbon, but in the incandescence of heavy hydrocarbon vapours.

In a paper read before the Chemical Society in January last, I described experiments and analyses which showed that the main reaction leading to luminosity in a flame containing hydrocarbons was the conversion in the inner non-luminous zone of the hydrocarbons into acetylene,—a change brought about by the baking action of the heat evolved by combustion in the outer layer of the flame, and in no way dependent upon oxidation, the change being entirely brought about by heat, as can be shown by passing the various gaseous hydrocarbons present in illuminating gases through heated tubes.

If an ordinary flat-flame be taken and the gases be carefully withdrawn from the non-luminous zone and analysed, the ratio of the acetylene formed, to the other unsaturated hydrocarbons, will be found to rapidly increase in their passage up the centre of the flame:—

Acetylene formed in the Inner Zone of a Flat-Flame from a No. 7 Bray Burner.

Portion of flame.	Total unsat. hydrocarbons.	Acetylene.	Other unsat. hydrocarbons.
	Per cent.	Per cent.	Per cent.
$\frac{1}{2}$ an inch from top of burner	3.565	0.115	3.450
$1\frac{1}{2}$ inches from burner ..	2.063	1.303	0.760
$1\frac{3}{4}$ " " " ..	1.393	1.133	0.260
$2\frac{1}{2}$ " " " ..	trace	trace	—

Showing that by the time the top of the non-luminous portion of the flame is reached over 81 per cent of the hydrocarbons present are converted into acetylene.

In such a flame luminosity commences just above the

inch and three-quarters above the burner, and if luminosity is caused by acetylene it is natural to ask why should it not have commenced at an inch and a quarter,—a spot where the acetylene is present in larger quantity than at the higher point. The reason for this is that in order to cause luminosity a temperature must be obtained at which the acetylene is dissociated, and the point at which this takes place marks the commencement of luminosity. If this temperature is not attained, then the acetylene in the presence of oxygen burns away with a non-luminous flame, or if no oxygen is present, polymerises into a number of higher hydrocarbons. If, on the other hand, a sufficiently high temperature is reached to cause dissociation, the liberated carbon becomes incandescent chiefly from its own combustion, but partly also from the combustion of the hydrogen liberated at the same time, and luminosity is the result.

The temperature needed to cause the dissociation of acetylene varies with the amount of dilution; the more diluted it is the higher being the temperature necessary to break it up, whilst the larger the quantity of acetylene the lower the temperature needed to cause its dissociation, and the smaller therefore the inner non-luminous zone of the flame.

In the flame from ordinary coal-gas there is only from 1.1—1.3 per cent of acetylene found in the inner zone, and in this highly diluted condition it requires a temperature of close upon 1200° C. to break it up, whilst in other flames richer in hydrocarbons, and therefore richer in acetylene in the inner zone, the temperature required is not so high; for example:—

Flame of—	Coal-gas.	Paraffin lamp.
Percentage of acetylene	1.133	2.222
Temperature at commencement of luminous zone	1267°	1062°

The fact that unless the requisite temperature is reached the acetylene burns away with non-luminous combustion is, I think, clearly shown by the following experiment.

The flame of burning alcohol contains more than half the quantity of acetylene that a good gas-flame contains, and yet the combustion is practically non-luminous. If a dish containing some alcohol be placed under a bell jar it burns with a flame having slightly luminous edges, and the temperature of the flame in this condition is 1220° C. If now a glass plate be put over the mouth of the bell jar for a few moments, the mixing of the products of combustion with the air lowers the rate of combustion, and the temperature of the flame falls to 1050° C., the flame becoming perfectly non-luminous, whilst if oxygen be admitted to the bell jar the combustion is increased and the temperature rapidly rises to 1510° C., the flame becoming nearly as luminous as a coal-gas flame, and depositing carbon on any cold surface held in it.

Again, if a small luminous gas-flame be allowed to play upon the bottom of a platinum dish, so much heat is abstracted from the flame that the temperature falls below the point necessary to break up the acetylene and the flame becomes non-luminous, whilst if the flame is allowed to remain in contact with the metal until the dish is red-hot the luminosity returns, and the same effect may be produced by heating the interior of the dish with a blowpipe flame. (This experiment was, I believe, devised by Heumann to show the effect of cooling on luminosity).

In every flame that I have examined which owes its luminosity to the presence of hydrocarbons, these bodies are converted into acetylene before luminosity commences in the flame, and every gaseous hydrocarbon which can by heat be made to deposit carbon is converted into acetylene before any deposition takes place.

Many of the hydrocarbons present in coal-gas are known to give out heat during their decomposition, but probably the most endothermic of these compounds is the acetylene, Thomsen having shown that no less than

* Read before the British Association, Edinburgh Meeting, 1892, Chemical Section.

55,020 units of heat are absorbed in the formation of 26 grains of acetylene, whilst only 10,880 disappear in the production of 28 grains of ethylene, and it is this which renders its decomposition by heat, or as shown by Berthelot, even by detonation into carbon and hydrogen, so easy.

The fact that acetylene is formed from the gaseous hydrocarbons present in illuminating gas prior to the emission of light does not, however, by itself in any way disprove Dr. Frankland's theory that luminosity is due to very heavy hydrocarbon vapours and not to solid particles of carbon, as the well-known tendency of the acetylene to polymerise into higher bodies might be taken as an explanation of the presence of sufficiently dense hydrocarbons in a flame given by, say, pure ethylene.

In order to determine whether or no the acetylene formed in the earlier stages of the flame renders the flame luminous by liberating carbon during dissociation as required by Davy's theory or by forming heavier hydrocarbons, a long series of experiments were made to ascertain the effect of heat upon the hydrocarbons present in coal-gas, and by specially devised apparatus to measure the actual temperature to which the gases were being heated, and to collect and analyse the resulting products. These experiments are still proceeding, but I may state the main results of them as being as follows:—

Ethylene passed at the rate of 4 to 5 c.c. per minute through a tube 2 inches in internal diameter undergoes no apparent change until the temperature rises to between 800° and 900° C.; it then breaks down to methane and acetylene; and simultaneously, with the formation of acetylene, heavy vapours appear which can be condensed, and in which benzene and naphthalene are conspicuous as well as a heavy and highly fluorescent oil of high boiling-point. Berthelot found that these substances were formed when acetylene was heated for some time at the temperature at which glass softens, and he also recognised among the products cinnamene, C_8H_8 , and retene, $C_{18}H_{18}$, so that there seems very little doubt but that in passing the ethylene through a heated space in which the temperature does not rise above 900° C., methane and acetylene are first found and the latter at once polymerises into the heavier hydrocarbons. The amount of acetylene found in the products of the experiment of this temperature rarely exceeds 1 per cent, as the polymerisation occurs almost simultaneously with its formation, but the proportion of ethylene decomposed and the amount of methane found in the products of decomposition point to the initial action of heat at this temperature being: $3C_2H_4 = 2(C_2H_2) + 2(CH_4)$.

On increasing the temperature from 900° C. slowly up to 1000° C. the same action continues, no hydrogen appears in the products of decomposition, and no carbon is deposited, but the formation of oil and solid hydrocarbons is more abundant. Between 1000° and 11,000° C. a trace of hydrogen appears and a little carbon begins to deposit with the oil, this increasing with rise in temperature up to between 1300° and 1400° C., by which time all formation of oil has ceased. Carbon is deposited in larger quantities, and the residual gas consists of hydrogen with a little methane. The temperature at which oil disappears is about 1200° C., and the proportion of acetylene formed at this temperature is larger than at any of the lower ones.

It is evident, therefore, that if the temperature existing in the luminous portion of the flame exceeds 1200° C. the luminosity cannot be due to such hydrocarbons as are formed from the acetylene, but that carbon will be present in abundance.

I have made several analyses of the carbon so deposited and find that the hydrogen in it varies from 1 to 3 per cent, and as there is no fixed ratio, I think there is not the slightest foundation for imagining that it is in combination; indeed, Stein's work upon this point is fairly conclusive, and anyone who has attempted to prepare hydrogen free carbon from sugar, or other similar body,

will realise the intense power which freshly liberated carbon has of occluding and holding hydrogen.

Ethane, which is present in illuminating gas in larger proportion than is generally supposed, breaks up even below 800° C. into ethylene and hydrogen—



and the ethylene behaves as before on increase of temperature. Methane, which is only present in very large quantities in the original gas, but is also produced during the decomposition of the ethylene, is apparently unaffected by heat until a temperature of 1000° C. is reached when hydrogen and unsaturated hydrocarbons begin to appear in small traces. Acetylene being the chief of these, this action continues and increases, so that at about 1500° C. considerable quantities of acetylene are formed which at once break down to hydrogen and carbon. With methane, as with ethylene, the first trace of acetylene found in the products is also accompanied by the formation of oils and heavy condensable vapours. Methane is not so easily converted into acetylene as the other hydrocarbons, and requires a higher temperature to bring about the change; but the fact that it does so at high temperatures fully explains the facts first observed by Dr. Percy Frankland and Mr. Lewis Thompson, that although methane when burnt by itself has but a very feeble power of illumination, yet that when used as a diluent of heavier hydrocarbons it greatly increases the light emitting power of the flame.

In order to apply the knowledge these experiments give of the changes taking place in the hydrocarbons present in coal-gas during their flow through the heated channel in the interior of the flame, it is necessary to map out the temperatures existing in a luminous flame, and the flat-flame from a Bray burner (No. 7) lends itself conveniently to this purpose.

Using the Le Chatelier thermo-couple described by Dr. Roberts-Austen at the last meeting of the British Association, and making only one short twist of the wires to give contact, and then coating them with hard glass, it is possible for nearly a minute to get the temperature in the portion of the flame in which the short twist is plunged, and if thin wires are used the loss by conduction is very small. Of course, if the part of the flame through which the glass coated wires pass are at a higher temperature than the portion around the twist, as the heat penetrates the glass it will give too high a reading, but for the first thirty or forty seconds there is no fear of this.

With this arrangement I was able to map out the temperatures existing in the flat-flame, in which I had traced out the changes taking place in the constituents of the gas; and I found that the temperature rapidly rose from 500° C. half an inch above the burner to a little over 1200° C. at the commencement of the luminous zone—the luminous edges having a temperature of 1216° C.; and these temperatures were further increased in the luminous zone until near the top of the flame 1368° C. was reached. This at once gives us the secret of the luminosity. From the mouth of the jet and up to a temperature of 1000° to 1200° C., we have the formation of acetylene from the original hydrocarbons; but the moment the requisite temperature is reached by the combustion of the hydrogen and the carbon monoxide, the acetylene decomposes with a further rise of temperature, and the carbon, heated to incandescence, radiates heat and light.

In the experiments with the hydrocarbons the gases were passing through a heated space six inches long kept at a constant temperature; in the flame they are passing through a space 1.75 inches long with a rapidly increasing temperature, so that instead of the acetylene becoming polymerised to any great extent, it reaches a temperature at which dissociation takes place almost immediately it is formed.

Experiments with hydrogen-borne benzene vapour show

that at a temperature of 1200° to 1300° C. it is reconverted to acetylene, and this then at once breaks down to carbon and hydrogen, and the same happens with any other heavy vapours formed in the inner zone, and these bodies formed probably in minute quantities by polymerisation, together with any remaining methane, are reconverted into acetylene and deposit their carbon as soon as the necessary temperature is reached, and this supplies a fresh quantity of carbon particles to the upper portion of the luminous zone and so increases its size.

The careful analyses of Hilgard, Landolt, and Blochmann, made to determine the interactions taking place in various flames, are in their main features in close accord with a long series of analyses of the flame gases which I have made, and one of the most striking features of these is the comparatively slow rate at which the heavy hydrocarbons disappear, as compared with the other constituents of the original gas. This I find to be chiefly due to diffusion, which causes the hydrogen and methane to find their way to the outer skin of the flame first, and it is these bodies, therefore, which bear the brunt of the earlier combustion and yield the heat which bake the heavy hydrocarbons ascending straight upwards from the burner into acetylene.

If three concentric tubes be placed half an inch above an open tube from which coal-gas is issuing, and the gas from each is withdrawn and analysed, it will be found that on comparing them with the original gas the action is most marked. The gas in the outer tube being practically a mixture of air with hydrogen and methane and no heavy hydrocarbons, whilst in the inner tube the unsaturated hydrocarbons have risen from 3.56 to 4.53.

All analyses of the flame gases also show that the hydrogen burns first, and that next in rapidity of burning is the methane, and Prof. Smithells advances the theory that in the incomplete combustion taking place in the flame the hydrocarbons burn to carbon monoxide and hydrogen.

As has been already shown, the proportion of heavy hydrocarbons consumed before conversion into acetylene and then dissociation into carbon and hydrogen is very small, and the principal hydrocarbon undergoing combustion in the flame is methane. The analyses of Landolt, Hilgard, Blochmann, myself, and Smithells all show that a large increase in the carbon monoxide undoubtedly does take place; the higher one ascends in the flame until the luminous portion is reached, and also it is probable from the same analyses that hydrogen is generated by some action in the outer layer of combustion, as in spite of its rapid combustion at the base of the flame, as shown by the large percentage of water vapour formed there, it keeps reappearing for some little distance up the flame, and it is to explain the joint appearance of carbon monoxide and hydrogen that Prof. Smithells brings forward the theory that carbon burns to carbon monoxide, setting the hydrogen free from the hydrocarbons.

There is not the slightest doubt from the work done by Dalton, Blochmann, Kersten, E. von Meyer, and Dixon, that if you explode together gaseous hydrocarbons with a limited supply of oxygen you obtain carbon monoxide and hydrogen, and it is also probable from H. H. Baker's experiments that carbon burns first to carbon monoxide, but I fail to see that any such theory is necessary to explain the actions taking place in a flame. If we analyse the gases present in the flame $\frac{1}{4}$ of an inch above the burner, which is about the point at which increase of carbon monoxide commences, although it is not marked until $\frac{1}{4}$ inches up the flame, we find that in the outer zone of the flame we have—

Water-vapour	24.65 per cent.
Methane	8.35 ..

A little deeper in the flame we get—

Water-vapour	17.94 per cent.
Methane	21.51 ..

and from this point up to $\frac{1}{4}$ inches you have the temperature rapidly rising from 750° C. to 1100° C., and it is a well-known fact that if heavy hydrocarbons and water vapour are heated together they yield carbon monoxide and hydrogen; indeed, it is the most expensive method of making water-gas, and wrecked one process for the manufacture of illuminating water-gas, and one would expect the same thing to happen when methane and water-vapour are heated to this temperature.

In order to try if this were so, methane was passed through water just below the boiling-point and then through a tube heated to 1000° C., the resulting gases being then analysed, when it was found that the methane and water-vapour had interacted to form hydrogen, carbon monoxide, and carbon dioxide, and I should think that this is a far more likely cause of the effects produced in the flame.

Taking the facts which I have now laid before you, we may, I think, fairly fully explain the actions that take place in the flame and lead to luminosity. As the gas leaves the jet, the hydrogen rapidly diffuses to the outer edge of the flame and burns, the methane doing the same but rather more slowly. The combustion of these gases raises the temperature 500° C. in the first half inch, while before another half inch has been traversed 1000° C. is reached, and the chemical changes in the hydrocarbons are progressing rapidly, the unsaturated hydrocarbons and higher members of the saturated hydrocarbons being rapidly converted into acetylene. If the temperatures of the flame were not allowed to rise above 1000° C. this acetylene would be nearly all polymerised into benzene, naphthalene, diphenyl, and other complex bodies, which would be slowly burnt up without liberation of carbon, and a non-luminous flame would result. In the case of a gas flame, however, instead of remaining at 1000° C. the temperature rapidly rises to 1200° C., with the result that instead of polymerising into more complex bodies most of the acetylene formed at once splits up into carbon and hydrogen, and the former heated to incandescence by combustion gives the luminosity. It is the attainment of this temperature that marks the limit of the non-luminous zone. If this were the only action, however, the luminous zone would be very short. The bodies, however, formed from the acetylene before 1200° C. was reached, and the methane, of which some still remains unburnt, are converted into acetylene at a still higher temperature, i.e., 1300° C., and this being reached near the top of the luminous zone yields a fresh supply of carbon, and so increases the height of the light-yielding portion of the flame.

In producing the luminous flame, therefore, there are two main factors to be observed: first, to use such compounds as shall be most easily converted into acetylene, and secondly, to attain as quickly as possible as high a temperature as practicable.

A NEW METHOD FOR MEASURING THE PRESSURE PRODUCED IN GASEOUS EXPLOSIONS.*

By BEVAN LEAN, B.A., B.Sc.,
Dalton Chemical Scholar of the Owens College,
and W. A. BONE, B.Sc., Fellow of Victoria University.

THE authors have devised a new method by which they hope to be able to measure the pressure produced on the explosion of gaseous mixtures. All former measurements involve the motion of a guage of considerable mass. Bunsen measured the pressure developed by studying the limiting weight raised by a valve attached to a bomb. Berthelot and Vieille determined the rate of displacement

* Read before the British Association, Edinburgh Meeting, 1892, Section B.

of a piston of known section and mass. Mallard and Le Chatelier have employed a Deprez manometer, and also a metallic Bourdon gauge. Dugald Clerk has made use of a Richards indicator. In consequence of the instantaneous character of gaseous explosions it is doubtful whether, by the means employed by these experimenters, it is possible to measure the *real* pressure produced by the explosion. Their methods would appear to measure no more than the effective pressure.

The authors announce preliminary experiments in which they have studied the pressure produced by a mixture of two volumes of hydrogen with one volume of oxygen.

They attached to a leaden coil of two litres capacity a strong glass tube of from 10 to 25 c.c. capacity, closed at one end, and separated at its other end from the coil by a gas-tight steel cap, the bore of which had the same diameter as the glass tube. The glass gauge had previously been calibrated and graduated. The coil was then filled with the explosive mixture, while the glass gauge was filled with air or hydrogen. The instant the mixture was fired the tap separating the coil from the gauge was opened, and the flash due to the exploding gases darted into the gauge. The experiment consisted in taking a photograph upon a sensitive plate of the flash in the gauge. It was found possible to obtain photographs which showed the flash to come to a well-defined and abrupt termination, marking the volume into which the air in the gauge had been compressed. By this means the authors hold that the air in the gauge is compressed adiabatically, and with the data afforded by the photograph they contend that it is possible to calculate the pressure produced in the explosion by Rankine's well-known formula—

$$P' = P \cdot \left(\frac{V}{V'} \right)^{\kappa}.$$

The assumption is therefore made that there is no loss of heat up to the time that the flash attains its furthest limit. To obtain some data to justify this assumption, the authors took a photograph of the flash upon a swinging plate attached to a pendulum chronograph. The plate moved past the flash at the rate of 2½ metres per second. The photographs so obtained could scarcely be distinguished from those taken upon a stationary plate; they were perfectly symmetrical, only the slightest possible increase in breadth could be detected. These photographs showed that the compression is approximately instantaneous, and that the flash ceases to have any sensible photo-chemical action in an interval of time less than one five-thousandth of a second. In so short an interval of time the compressed gas cannot lose a sensible quantity of heat. It would appear, therefore, right to assume that the compression is adiabatic. The authors believe also that no appreciable diffusion of the compressed gas into the compressing gas can occur during the very brief time of compression.

Further, since thermo-dynamic theory proves the ratio of the two specific heats of any perfect gas to be approximately constant for all temperatures and pressures, Rankine's formula may be employed to calculate the pressure produced by the explosion when the gauge is filled with air or hydrogen.

Essentially, therefore, the method gives a record of the adiabatic compression of a gas by the explosion, a piston of indefinitely small thickness and mass being interposed between the compressed and compressing gases.

Experiments have been made with gauges of different volume, varying from 11.55 c.c. to 23.20 c.c., and the ratio $\frac{V}{V'}$ is found to be independent within these limits of

the volume of the gauge. Further, the ratio $\frac{V}{V'}$ is found to be the same, within the error of experiment, whether air or hydrogen is the gas compressed. The photographs obtained, however, in the case of hydrogen, show the flash to be in general ill-defined and pointed, owing

probably to the high thermal conductivity of hydrogen, combined with a much greater inter-diffusion with the compressing gases in consequence of the greater molecular velocity of hydrogen in comparison with that of hot air.

The mean value from six different sets of experiments with air and hydrogen, electrolytic gas being the explosive mixture, gave $\frac{V}{V'} = 8.6$. Calculating P' by means of

Rankine's formula, and taking $\kappa = 1.408$, it is found that $P' = 20.7$ atmospheres. This pressure is about twice that measured by former experimenters. Some experiments were also made with carbonic acid gas; in these the explosion compressed the gas into a much smaller volume, owing to the great variation of the two specific heats of carbonic acid gas with increase of temperature and pressure.

The authors desire to state that the idea upon which their method is based was suggested to them by Professor H. B. Dixon.

WATER ANALYSIS.

By J. ALFRED WANKLYN.

FROM a letter of Dr. Frankland's which has been recently published it would appear that that eminent chemist (who succeeded the late Mr. Way as chemist on the Royal Commission on the Pollution of Rivers, and the late Professor Hofmann, as chemical contributor to the Registrar General's Annual Report) has quite recently been made Chemical Adviser to the Local Government Board. It would seem, moreover, that in this last official capacity he has been employed in endeavouring to disparage and discredit the ammonia process and in forcing his own process upon reluctant analysts. Under these circumstances I have to take up the controversy which was carried on at the meetings of the Chemical Society in the years 1868 and 1876; and to urge afresh the reasons against Dr. Frankland's process and in favour of our process.

Dr. Frankland's process consists in taking a given quantity of water, evaporating it down to dryness (the nitrates being reduced during the evaporation by sulphurous acid), and finally performing elementary organic analysis on the water residue. From the carbonic acid so obtained the carbon is calculated and called "*organic carbon*," and the nitrogen gas so obtained is measured and called "*organic nitrogen*"; and these two data are, if Dr. Frankland is allowed to have his way, to become the criteria of the purity or otherwise of drinking water. I believe it would be most disastrous and injurious to the good name of English chemists if such an event should take place, and will now recall to mind the objections to the Frankland water analysis.

The first objection is that the process, as he works it, is invalid. It will be obvious to most people that a process which burns up a water residue and confines itself to measuring the carbonic acid and nitrogen so generated cannot measure the carbon and nitrogen in any organic matter which volatilises during the evaporation of the water. Equally obvious to most people will it be that in so far as the non-volatile organic matter undergoes decomposition during the evaporation, in so far it will be liable to escape registration when the water residue is submitted to the final combustion. Frankland's process is in fact confined to such organic matter as survives the evaporation, and at its best could only give the organic carbon and organic nitrogen in water residues—which is a very different thing from the organic carbon and nitrogen in the original water.

Now, having obtained a dry water residue, free from carbonates and nitrates, there would be no difficulty in ascertaining the actual weight of carbon or nitrogen by applying to it the ordinary elementary organic analysis, which is one of the best known, and most accurate and

trustworthy of all processes. But elementary organic analysis is only valid when certain essential conditions are complied with. Chief among such conditions is that the combustion should be carried out on a proper scale—that the burning of too little organic matter should be avoided. Frankland burns up the residue from one litre (and I believe in some instances from less than one litre of water), but the organic matter in the water residue from one litre of drinking water is too little to give a real result, and the failure to operate upon a sufficiently large water residue renders his water analysis invalid, even as a process for the ascertainment of the organic carbon and nitrogen in a water residue.

Now it may be asked why should not Frankland evaporate down ten litres instead of only one litre, and so obtain a residue which would contain enough organic matter? In a week or a fortnight at the outside the evaporation of ten litres might be accomplished without being obliged to increase the size of the evaporating dish. To Dr. Frankland time and trouble and cost are of no account.

The real reason against any increase of the scale of the operation is that it would bring Dr. Frankland face to face with an irresistible proof of the fundamental and inherent vanity of his water analysis. Nothing is more likely than that the water residue from ten litres of common drinking water would contain as much organic carbon and nitrogen as could be got from the residue of twenty litres of the same kind of drinking water. I fancy that Dr. Frankland feels that something of that kind would happen, and that his faith in his own process would vanish along with the organic matter, which would suffer destruction on prolonged evaporation of many litres of drinking water.

Instead of burning the water residue left by many litres of water, and in that manner complying with the condition essential to the genuineness of the results, Dr. Frankland has sought so to modify the process of elementary organic analysis as to diminish the quantity of organic matter required for combustion. Fortunately, he published ten examples wherein small quantities of sugar, urea, and hippuric acid were burnt, and, as I pointed out at the meeting of the Chemical Society in the year 1868, the fact came out plainly enough that his modification of elementary organic analysis had not effected any real diminution of the error of experiment. His apparatus for the measurement of nitrogen and carbon would indicate 0.001 m.grm. of nitrogen and 0.0005 m.grm. of carbon; but the actual practical error of experiment as exhibited in his test analyses amounts to tenths of a m.grm., and even to a whole m.grm.; and in calling attention to it at the time, I could not help remarking that the actual performance appeared to be a satire upon his beautiful instrument.

In the practical working of his process, each analyst is directed to perform several blank operations "so as to be able accurately to correct for the combined errors of his own manipulation and apparatus." In Frankland's laboratory the correction actually came up to 0.32 m.grm. of carbon and 0.045 m.grm. of nitrogen per litre of water. A personal error of that magnitude is a satire on measurements claiming to be accurate to the thousandth of a m.grm. Persistent working where the personal error is so large and the measurements so delicate, and where, moreover, the operations are so tedious and laborious that they have to be almost wholly entrusted to assistants, leads to strange results, and in due course landed the Royal Commission on the Pollution of Rivers at the celebrated experiments on sulphate of quinine, which formed the subject of a correspondence in the *CHEMICAL NEWS*. In those experiments certain quantities of sulphate of quinine were dissolved in water, and the solutions of quinine were evaporated to dryness and the residues burnt, and the organic carbon and nitrogen arrived at. The experimental carbon and nitrogen agreed exactly with the calculated quantities, but the calculated quantities were wrongly calculated. And in that manner

the real nature of the results flowing from the Frankland water-analysis was exhibited in a most striking manner. Nothing, however, is more conclusive than the results of the examination of the water of Bala Lake. This water was at one time thought of as a possible supply for London, and punctually the Frankland method exhibited organic nitrogen 0.01 m.grm. per litre. Bala Lake water is not by any means pure water. It yields 0.25 m.grm. of albumenoid ammonia per litre, and the real quantity of nitrogen existing in organic combination in a litre cannot have fallen short of 0.20 m.grm.

New Malden, Surrey,
Aug. 16, 1892.

ANALYSIS OF COPAL RESINS.

By ED. KRESSEL.

(Continued from p. 91).

THE melting-point of copal resins varies from 175° to 370° C. When carefully roasted, at first a small quantity of gas, about 4 to 5 per cent, is obtained, which consists of—

	I.	II.
CH ₄	40.30	41.27
CO ₂	23.57	23.85
CO	36.13	34.88
	100.00	100.00

Heating further the copal oil distills over. I have made many careful experiments in order to estimate what loss in weight must occur before a soluble resin, fit for further manufacture of varnishes, can be obtained, and I have found it to be on an average from 8 to 12.5 per cent, but when the roasting process is carefully conducted, the loss need not exceed 10 per cent, and the raw product is fully converted into the soluble "pyro-copal."

Naturally when a closed vessel is in use for roasting the vapours are condensed, the copal oil thus collected and used otherwise. It must not be understood that the solubility of a copal resin depends upon the absence of the copal oil or a certain portion thereof, for we have seen before, on extracting the copal oil with ether from the raw copal, the swell copal was left as an insoluble matter, and still required the necessary high temperature to be converted into the soluble pyro-resin.

When the melting-point is reached the heat should so be regulated that the temperature does not increase by any way and be only slowly kept up; the mass will soon flow evenly, and after about 15 to 20 minutes the whole is sufficiently treated to be ready for further manufacture. Certainly the time is calculated for about 10 to 12 pounds of raw copal, and more time would be required should larger quantities be treated at once.

Quite analogous with this process is the conversion of starch into soluble dextrin; the former is heated to about 150°, and if a small quantity of HNO₃ or HCl is added to the starch the transformation takes place much more rapidly. This is also the case with copal, though on this point I will speak later on, as my investigations are not completed in that way at present.

The analysis of the carefully roasted (at 352° C.) soluble product, "pyro-copal," gave:—

	I.	II.	Average.
C	83.29	83.05	83.17
H	10.55	10.73	10.64
O	6.16	6.22	6.19
	100.00	100.00	100.00

The heat increased to 365° C.—

	I.	II.	Average.
C	84.23	84.37	84.30
H	10.76	10.73	10.745
O	5.01	4.90	4.955
	100.00	100.00	100.00

The heat increased to 375° C.—

	I.	II.	Average.
C.. ..	85'05	85'07	85'06
H.. ..	10'85	10'85	10'85
O.. ..	4'10	4'08	4'09
	100'00	100'00	100'00

From the chloroform solution of pyro-copal alcohol precipitates the pyro-swell copal. The substance dried at 100° C. gave—

	I.	II.	Average.
C.. ..	82'87	82'85	82'86
H.. ..	10'63	10'78	10'705
O.. ..	7'50	7'37	7'435
	100'00	100'00	100'00

Comparing now the raw copal with the pyro-copal and the swell copal with the pyro-swell copal, we find that roasting causes in every instance an increase of C. and a decrease of O, while the H remains nearly constant.

ON THE DISSOCIATION OF ELECTROLYTES IN SOLUTION AS SHOWN BY COLORIMETRIC DETERMINATIONS.

By H. M. VERNON, B.A.

WITHIN recent years theories have been advanced by Kohlrausch, Ostwald, and others, as to the state in which salts exist in solution, which at first sight appear to be startlingly contradictory to all previous ideas on the subject, and which might well be considered to revolutionise chemistry. So numerous and so powerful are the proofs in favour of these theories, however, that in spite of many seeming objections one can scarcely doubt their validity. Each new series of experiments made on the subject seems to afford an additional proof; it is hoped that the results of the experiments detailed in this paper may be considered as still another.

If a dilute solution of a coloured salt—as copper sulphate, for instance—contains less molecules of copper sulphate as such than a more concentrated solution, owing to dissociation of the salt into its ions Cu and SO₄, it follows, if no other influences are at work, that with equal quantities of salt present in each solution, the colour of the dilute solution must be lighter than that of the more concentrated solution, and that, too, in proportion to the amounts of copper sulphate molecules dissociated into their ions. It is possible that the ions themselves of coloured salts may form coloured solutions, and so the colour of a dissociated salt may not be any different from that of the undissociated salt. The probability of this being the case will be discussed further on. If, however, experiment actually shows that dilute solutions of coloured salts are more than proportionately light in colour than concentrated solutions, there is a great probability that it is due to dissociation in solution. To test this, solutions of some thirty-five coloured salts were compared with each other colorimetrically at different dilutions. The influence of temperature on the colour effects of the different solutions was also determined.

The colorimeter used consisted of two graduated glass tubes with flat bottoms about 2.5 c.m. in diameter. One tube had a tubulure near the bottom, connected by india-rubber tubing to a vessel capable of being moved up and down vertically in a clamp, so that the volume of liquid in the tube could be altered at will. Each of the tubes was carefully calibrated, and the corrections to be applied for each volume in both the vessels determined. The required volume of the more concentrated of the two solutions to be compared was run from the burette into the non-tubulated vessel, and the volume of liquid in the

tubulated vessel varied till of the same tint. The two tubes stood on a plate of clear glass, and light was reflected up the tubes from underneath by a sheet of white paper stretched on a plate arranged at the angle reflecting the greatest quantity of light. A sheet of paper is much to be preferred to a plate of white porcelain or to a mirror, as these reflect images of any objects coming across their path, and so do not give a uniformly illuminated surface.

All colour comparisons were made at a window through which no direct sunlight entered. The solutions in the two tubes were viewed vertically from above through a piece of white cardboard with two circular holes cut in it, so that two uniformly illuminated surfaces of the solutions were seen. It was found that with practice colours could be judged correctly in almost all cases to within three per cent, and, as in comparing solutions at different dilutions, four or more separate observations with different volumes of solution were made, the values are in most cases accurate to within two per cent or less. After getting the solutions as nearly of the same tint as possible, it was found best to turn the eye to some different object altogether, especially one of a colour complementary to that of the solution under examination, and then after a few seconds to again examine the solutions, when it was frequently found that they were not accurately compared the first time. The same process was repeated twice more before the comparison was finally considered as correct. With deeply coloured solutions, the mask through which the solutions were viewed was protected from the light by a shade, when, from contrast with the now darkened mask, the comparison was rendered much more easy. With very dilute solutions, the intensity of the light reflected up the tubes was decreased by interposing a piece of tracing paper in the path of the light from the window. The salts used were not specially purified, but the purest specimens obtainable from the manufacturers were always used.

The Change of Colour Effect on Dilution.

The method of procedure was as follows:—100 c.c. of the normal solution was made up, and 25 c.c. of this was diluted to 125 c.c., whereby a solution of 5 litres dilution was obtained; 7 c.c. of the normal solution was introduced from a burette into the non-tubulated vessel, and the colour comparison with the 5 litres solution made; 3 c.c. more of the normal solution was then introduced, and another comparison made, and so on. A decinormal solution was then made up and compared with the normal solution. Centinormal solutions were compared with the decinormal, and millinormal with the centinormal.

The salts examined consisted of the sulphates, chlorides, and nitrates of the metals copper, nickel, cobalt, chromium, and uranium, together with the acetates of three metals, and also several organic salts of iron. These salts were chosen in order to determine whether any general relations existed between the changes of colour effect on dilution and the nature of the acids and bases composing the salts.

Five copper salts were examined. From the table it will be seen that the solutions of all the salts decrease in colour effect on dilution, the sulphate the least, then the chloride, chlorate, nitrate, and lastly the acetate, which decreases very greatly on dilution. The reason of this will be indicated further on. None of the salts of either copper, nickel, cobalt, or uranium showed deep enough tints to make determinations at dilutions of 1000 litres possible. Nickel salts show much less colour decrease than copper salts, neither the sulphate nor the chloride showing more than a barely appreciable decrease at a dilution of 10 litres. All the cobalt salts dissociate considerably more than the corresponding salts of both nickel and copper; but in this case, though the sulphate is the least dissociable, it is the chloride and not the nitrate that is the most dissociable. The same thing holds for uranyl salts, the sulphate being less dissociable than the nitrate, and this again than the chloride. These

Substance.	Colourations at dilutions.							Dilution in litres.	Chromium sulphate.	Chrome alum.	Chromium chloride.	Cobalt sulphate.	Iodine.
	1.	2.5.	5.	10.	50.	100.	1000.						
Cupric sulphate ..	100	—	98.3	95.1	—	93.0	—	10	100	100	100	100	100
„ chloride ..	100	—	98.4	91.0	—	88.2	—	20	100.7	96.6	100.9	97.5	95.0
„ nitrate ..	100	—	87.4	85.9	—	81.2	—	30	101.3	92.7	100.0	92.0	94.7
„ chlorate ..	100	—	90.7	89.6	—	84.9	—	40	98.9	92.2	99.1	90.5	93.5
„ acetate ..	—	100	82.7	68.2	—	37.1	—	50	98.2	93.8	98.0	90.0	90.7
Nickel sulphate ..	100	—	100.1	98.5	86.2	—	—	70	99.4	92.7	100.6	89.6	90.7
„ chloride ..	100	—	99.1	97.5	94.5	—	—	100	97.4	90.0	99.8	89.2	92.4
„ nitrate ..	100	—	97.3	94.1	83.2	—	—	120	96.0	87.4	100.1	87.8	93.8
Cobalt sulphate ..	100	—	90.8	89.2	—	77.8	—	150	95.8	87.5	101.1	86.5	94.0
„ chloride ..	100	—	87.9	76.4	—	65.5	—	180	96.1	85.6	100.4	85.7	94.5
„ nitrate ..	100	—	93.1	89.4	—	79.2	—	200	95.5	87.2	101.2	84.6	94.0
Uranyl sulphate ..	—	100	97.1	91.9	—	86.7	—	300	96.2	90.3	100.2	83.7	94.5
„ chloride ..	—	100	90.0	82.6	—	78.4	—	400	98.1	92.6	101.5	82.8	95.0
„ nitrate ..	—	100	98.1	90.9	—	85.6	—	500	99.0	90.8	103.0	82.0	95.3
„ acetate ..	—	100	98.5	96.9	—	92.1	—	600	103.0	92.0	104.3	80.7	96.1
Chrome alum ..	—	—	—	100	84.5	91.6	90.6	700	104.7	90.0	108.2	79.0	98.3
Chromic sulphate ..	—	—	—	100	94.4	99.8	91.1	800	110.2	90.6	—	78.5	98.2
„ chloride ..	—	—	—	100	98.6	94.7	90.6	1000	110.2	—	—	77.8	99.9
„ nitrate ..	—	—	—	—	100	121.8	107.2						
Iodine	—	—	—	100	—	95.2	115.2						
Potassium chromate	100	—	101.9	102.9	—	100.8	103.6						
Potassium bichromate	—	—	100	97.4	—	85.0	73.9						
Chromium trioxide ..	100	—	79.4	69.1	—	59.3	42.9						
Ferric chloride ..	100	—	160.5	208.3	—	246.8	—						
Ferric chloride + hydrochloric acid ..	—	—	100	70.5	—	16.3	5.4						
Ferric acetate	—	—	—	100	—	149.1	—						
„ citrate	—	—	100	101.3	—	133.2	—						
Ferric citrate + citric acid	—	—	—	100	—	131.1	176.7						
Ferric ammonium citrate	—	—	—	100	—	102.1	102.8						
Ferric oxalate	—	—	100	77.9	—	63.6	53.8						
„ tartrate	—	—	100	118.1	—	270.6	342.6						
Ferrous citrate	—	—	—	—	—	100	61.1						
Potassium ferrocyanide	—	100	98.8	97.2	—	—	—						
Potassium ferricyanide	100	—	98.1	93.5	—	89.1	88.5						
Potassium permanganate	—	—	100	103.0	—	103.8	96.8						

salts dissociate to a greater extent than copper salts, but not so much as cobalt salts. The acetate of uranium solution, however, shows a very different behaviour from that of acetate of copper, for it is the least dissociable of any of the uranyl salts examined. Chromium salts gave very extraordinary results, for the colour effect of their diluted solutions was found to depend on the method of dilution, according as it was sudden or gradual. Such results were afforded by no other solutions of salts examined. In the table are given the values obtained by diluting the solutions suddenly by adding all the water to the more concentrated solution at once. It will be seen that with solutions of chromium sulphate and chloride, and chrome alum, the colours at 50 litres dilution are considerably less than those at a dilution of 10 litres, but that on further dilution to 100 litres the colour increases, whilst it again decreases on still further dilution. Concentrated solutions of these three salts were then diluted gradually from 10 to 1000 litres, a colorimetric determination being made at each dilution. The results obtained were as follow in the table. The numbers in the last two columns will be referred to later on.

It will be seen that chromium sulphate solution decreases slightly in colour effect till a dilution of 200 litres, but that from this point it begins to increase again, till at 1000 litres it is considerably greater than the decinormal solution.

It is noticeable that the colour effects obtained by gradual dilution are quite different both in intensity and even in direction from those obtained by sudden dilution,

for with 1000 litres solutions in one case the colour effect is greater, and in the other less than the colourations of the 10 litres solutions. There is, however, a general resemblance between the colour effects of chromic sulphate and chrome alum solutions in the sudden dilution series, and also in the gradual dilution series. Chromium nitrate solution increases greatly in colour effect on sudden dilution from 50 to 100 litres, and decreases again on further dilution. These experiments with chromium salts were repeated, the same values being obtained, so they cannot be due to experimental error. Such extraordinary behaviour can only be explained on the supposition that hydrates of different composition and different colour effect are formed, according to the manner of dilution.

The only exception besides the chromium salts was found in the case of a solution of iodine dissolved in potassium iodide. The iodine was dissolved in a solution containing three times its weight of this salt. On dilution of the solution to 100 litres, the colour effect decreased, but after this point it began to increase, till at 300 litres dilution it had reached the value 107.3, and at 1000 litres that of 115.4. The solution was then examined by gradual dilution, when it was found that in the same manner the colour decreased up to a dilution of about 80 litres, and from this point began to increase again, but only slightly.

Both series of experiments were repeated and found to give the same results, so the variations cannot be due to experimental error. What they can be due to it is difficult to conceive. It may be that the decinormal solution contains a few molecules of I_2 , which up to a dilution of 100 litres are dissociated into I_2 molecules, but that on still further dilution these I_2 molecules begin to be dissociated into I molecules, with increase of colour effect. There are evidently two distinct reactions taking place in the solution; also it may be that the presence of potassium iodide in the solution has some influence, some peroxide being formed.

Several other salts were examined colorimetrically by gradual as well as by sudden dilution, but the same values were obtained in each case. The values found for cobalt sulphate are given as an example. The solutions are ten times more concentrated than the dilutions given.

(To be continued).

A New Stopper for Reagent Bottles.—A. Gawalowski.—The stopper has a mushroom shaped stopper to prevent dust from falling (nothing novel!), and is drawn out below to a point. A lateral cavity is ground in the lower part of the stopper to permit of the reagent being poured out in drops. The contact surfaces of the bottle and the neck are ground to prevent the stopper from sticking fast.—*Zeitsch. für Anal. Chemie*, xxx., Part vi.

ON THE
ESTIMATION OF URIC ACID IN URINE:
A NEW PROCESS BY MEANS OF
SATURATION WITH AMMONIUM
CHLORIDE.*

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THE process to be described depends upon the following facts:—

1. Ammonium urate is wholly insoluble in saturated solutions of ammonium chloride.

2. If solutions, such as urine, which contain the mixed urates of different bases be saturated with ammonium chloride, the large mass-influence of the latter ensures the rapid and complete conversion of all the uric acid into biurate of ammonium, which, in accordance with (1), is, *pari passu*, thrown out of solution. In the case of urine, saturation with ammonium chloride is followed by a complete precipitation of the uric acid present in the course of two hours at most.

It has long been known that ammonia and salts of ammonia will, after long standing, so completely precipitate the uric acid from urine, that subsequent treatment with acids produces no further precipitate (Wetzlar, "Beiträge zur Kenntniss des menschlichen Harns," Frankfurt a.M. 1821, p. 19). Fokker, moreover, observed that when a solution of any urate is made alkaline, and then mixed with a solution of ammonium chloride, the uric acid slowly separates out as the biurate of ammonia. Upon this observation the well-known Fokker-Salkowski process is based.

But the crucial fact that saturation with the ammonium chloride renders the separation rapid and absolutely complete does not seem to have been previously observed. The importance of this fact in any attempt to estimate uric acid by means of its separation as ammonium urate will be seen when it is remembered that, hitherto, in all such processes, a large correction has to be made to allow for incomplete separation, even after long standing. In the Fokker-Salkowski process, for instance, the factor which has to be added to the result amounts to at least 25 per cent of the total variably dealt with,—a necessity which would seem to render the process of little scientific value (*vide* Fokker, *Pflüger's Archiv*, vol. x., p. 157, 1875; Salkowski, *Virchow's Archiv*, vol. lxxviii., p. 401, 1876). In the method about to be described no such correction is necessary.

The following experiments with pure urates will show the complete separation of ammonium urate which occurs after saturation with the chloride.

In each case pure uric acid, prepared by means of the sulphate, was used. The ammonium salt precipitated was decomposed by means of HCl, and the uric acid subsequently washed and weighed, due allowance being made for washings:—

	Uric acid recovered.
(1.) One decigram. of uric acid dissolved in ammonia, solution made up to 250 c.c., saturated with ammonium chloride, and filtered after 30 minutes	0.0994
(2.) Fifty m.grms. dissolved as above and made up to 150 c.c. Filtered after 15 minutes	0.0502
(3.) One decigram. dissolved in Na_2CO_3 , solution made up to 100 c.c. Filtered after 3 hours	0.0986
(4.) One decigram. dissolved as in (3). Filtered after 4 hours	0.0990

The presence of excess of bases, other than ammonia, delays the precipitation, but, as stated above, two hours

is amply sufficient in the case of urine. (*Vide* note (b), *infra*).

The process of estimation in urine may be carried out as follows:—

To 100 c.c. of the urine, finely-powdered pure ammonium chloride is added in excess, about 30 grms. being necessary. The solution is allowed to stand for two hours, with occasional stirring, and the precipitate then filtered off through a thin filter paper.

The precipitate is then washed with a saturated solution of ammonium chloride. If a few crystals of the solid salt used for precipitation are still undissolved at the time of filtration, it is of no disadvantage; the light flocculent urate is easily washed first on to the filter, the crystals being then dissolved in a minimum of distilled water and used for washings.

After it has been washed twice or thrice with the saturated chloride solution, the urate is washed off the paper into a small beaker by means of a jet of hot distilled water.

The ammonium urate is then decomposed by boiling with a slight excess of HCl, the solution concentrated, if necessary, and the uric acid allowed to separate out. It may be finally determined by any accustomed method (*Vide*, however, note (c), *infra*).

Notes.

(a.) The ammonium chloride used must be pure. Since 30 grms. are used to precipitate 100 c.c. of urine, and only some 30—40 m.grms. of uric acid finally weighed, it is obviously fatal to the accuracy of the process if even a very small percentage of insoluble matter is present in the salt. In some samples, sold as pure, I have found appreciable quantities of sand, and in others, an amount of fibre from the filter used in the preparation of the salt equal to 2—3 m.grms. in the 30 grms. Other mineral salts of ammonia will precipitate the urate on saturation, but none are so satisfactory as the chloride.

(b.) The presence of free ammonia greatly accelerates the separation of ammonium urate after saturation with ammonium chloride.

The addition of AmHO to urine obviously involves the separation of phosphates. But, if the samples be first saturated with the chloride, and the hydrate subsequently added, the separation of urinary phosphates is greatly modified. No gelatinous precipitate comes down, but only a small quantity of triple phosphate crystals, such as neither adds appreciably to the bulk of the urate precipitate, nor increases the difficulty of filtration (this is rendered evident if the precipitate produced by AmCl in an acid urine be first filtered off and AmHO added to the filtrate).

If, therefore, time is of special importance, AmHO may be safely added after saturation with AmCl. The urate, *plus* phosphate, may now be filtered off within ten minutes, and the uric acid liberated in the usual way.

In describing the process above, standing for two hours is recommended where AmCl is added alone. In a very large percentage of urines, however, if not in all, one hour will be found enough.

(c.) The final determination of the separated uric acid may, of course, be carried out by means of weighing on a tared filter-paper, or on a Ludwig's glass-wool filter.

Personally, however, I greatly prefer to filter the crystals through a small filter of the kind sold by Schleicher and Schüll and called by them "Gebärtete" filter-paper. From these the uric acid may be very easily washed, without loss, into a weighed glass basin. The washings are then evaporated to dryness on the water-bath, the residue dried at 110° C., and weighed.

A Volumetric Method.—Recent experience has convinced me of the utility of permanganate solutions (*vide* Sutton's "Volumetric Analysis," 4th ed., p. 89) for the accurate titration of urates; so much so that I believe uric acid, once separated, by any method, from admixture

* A Paper read before the Royal Society, June 16, 1892.

with other organic substances, may be better titrated than weighed.

At temperatures ranging round 60° C. a perfectly determinate reaction occurs, involving the instantaneous decolourisation of the permanganate; and, though oxidation continues on standing greatly beyond the limits of this reaction, a perfectly definite end-point is obtainable, giving results which will be found extremely accurate.

The uric acid separated, as above, from 100 c.c. of urine is, after washing, dissolved by warming with a minimum of Na_2CO_3 . The solution is then cooled to about 15° C., made up to 100 c.c., transferred to a flask, rapidly mixed with 20 c.c. of pure strong sulphuric acid, and then immediately titrated with one-twentieth normal potassium permanganate solution. The addition of 20 per cent of sulphuric acid produces just such a temperature as is required for the reaction. The end-point is marked by the first appearance of a permanent pink flush. On standing, the colour continues to disappear, but this slow decolourisation is in marked contrast with the instantaneous nature of the first reaction. Careful experiments with pure urates have convinced me that uric acid may be thus estimated to within less than half a milligram.

One c.c. of twentieth normal permanganate of potassium, made by dissolving 1.578 grms. of the salt in 1 litre of distilled water, is equal to 0.00375 gm. uric acid.

In the "Guy's Hospital Reports," for 1891, I have described a method in which the ammonium urate precipitate, obtained by saturation with AmCl , is directly titrated with permanganate. As this precipitate always contains a trace of pigment, the results are somewhat high, but the method will be found sufficiently accurate for clinical purposes.

Evidence as to the Accuracy of the Ammonium Chloride Separation when applied to Urine.

1. After urine has been saturated with the chloride, allowed to stand, as described, and filtered, uric acid cannot be detected by any process in the filtrate.

2. The uric acid as weighed gave the following figures on combustion. Mixed residues from actual determinations were used:—

		Found.		Theory.
		(a).	(b).	
C		35.460	35.990	35.71
H		2.561	2.590	2.381
N		32.400	31.980	33.3

The above nitrogen figures show some variation from theory, but it should be remembered that elementary analysis is a very rigorous test when applied to such unpurified products. I have never obtained figures so near to the truth from the product weighed in the Ludwig process.

3. Comparison with the standard Ludwig-Salkowski process:—

Series I.

Sample.	M. grms. per 100 c.c.	
	Ludwig.	AmCl .
1.	23.0	23.0
2.	46.0	49.0
3.	55.0	57.5
4.	59.5	61.5
5.	64.0	68.0
6.	80.5	82.5

Series II.

7.	70.5	71.0
8.	54.5	54.5
9.	40.5	39.5
10.	40.0	40.5

The experiments in Series II. will be seen to afford nearer agreement than the earlier series, carried out be-

fore the same amount of experience had been obtained. The better agreement depends partly upon the use of a purer ammonium chloride, but chiefly upon a precaution in Ludwig's method to which reference is made below.

Notes on other Processes.

Having regard to the discussion at present going on with respect to the whole question of uric acid estimation, it may not be out of place to chronicle such experience of other processes as has been gained in the course of working out the method just described.

In comparing the ammonium chloride figures with those of Ludwig's process, the experiments marked Series I. above indicated an excess by the former method equal to some 3 m.grms. from the 100 c.c. of urine. As stated above, a part of this excess was due to impurities in the ammonium chloride, but it was mainly due, I believe, to a destruction of uric acid which occurs in Ludwig's process when the silver urate is treated with the alkaline sulphhydrate. It is, of course, well known that uric acid is decomposed on heating with caustic alkalies, but it is hardly recognised with what great ease the decomposition takes place. I find that, on boiling 50 m.grms. of pure uric acid briskly for five minutes with 10 c.c. of Ludwig's sulphide solution (*vide* Neubauer and Vogel, "Analyse des Harns," p. 543), i.e., the amount used to decompose the silver salt from 100 c.c. of urine, there is always an appreciable loss, sometimes amounting to 3 m.grms. It is therefore obvious that even five minutes' boiling would be fatal to the accuracy of an estimation. In Series II. above, the silver compound was thoroughly shaken up with the sulphide in the cold, and only just heated to boiling before filtration.

Mr. E. Groves, B.Sc., has recently described (*Journal of Physiology*, December, 1891) a modification of Ludwig's method which I have several times employed. Mr. Groves uses potassium iodide instead of the sulphide to decompose the silver urate. In my hands the method has always given results which are decidedly too low, owing doubtless to the action of the liberated iodine upon the uric acid in the acidified filtrate.

I have performed a large number of experiments with Haycraft's method, and have found that results obtained by its means are invariably too high, while the proportionate error undoubtedly appears to be variable. This appears to be the common experience. My own experiments, however, lend no support to the extraordinarily wide variations from the truth which some observers, especially in England, have ascribed to it. I should put the limit of error at from +10 to +15 per cent.

In conclusion, it may be claimed for the separation by means of saturation with chloride of ammonium that it yields results which are at least as accurate as those of Ludwig's method, while it is far easier to carry out, and occupies much less time.

METHODS FOR DETERMINING PHOSPHORIC ACID AND MOISTURE.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

1. *Preparation of Sample.*—The sample should be well intermixed and properly prepared and passed through a sieve having circular perforations one twenty-fifth of an inch in diameter, so that separate portions shall accurately represent the substance under examination, without loss or gain of moisture.

2. *Determination of Moisture.*—(a). In potash salts, nitrate of soda, and sulphate of ammonia heat 1 to 5 grms. at 130° C. till the weight is constant, and reckon water from the loss. (b). In all other fertilisers heat 2 grms., or if the sample is too coarse to secure uniform lots

of 2 grms. each, 5 grms., for five hours at 100° C. in a steam bath.

3. *Water-soluble Phosphoric Acid*.—Weigh out 2 grms. in a small beaker, wash by decantation four or five times with not more than from 10 to 15 c.c. of water, then rub it up in the beaker with a rubber tipped pestle to a homogeneous paste, and then wash four or five times by decantation with from 10 to 15 c.c. of water. Transfer the residue to a 9 c.m. No. 589 Schleicher and Schüll filter, and wash with water until the filtrate measures not less than 250 c.c. Mix the washings. Take an aliquot (corresponding to one-half grm.) and determine phosphoric acid as under total phosphoric acid.

4. *Citrate-insoluble Phosphoric Acid*.—Wash the residue of the treatment with water into a 200 c.c. flask with 100 c.c. of strictly neutral ammonium citrate solution of 1.09 density, prepared as hereafter directed. Cork the flask securely and place it in a water bath, the water of which stands at 65° C. (The water bath should be of such a size that the introduction of the cold flask or flasks shall not cause a reduction of the temperature of the bath of more than 2° C.) Raising the temperature as rapidly as practicable to 65° C., which is subsequently maintained, digest for thirty minutes from the instant of insertion, shaking every five minutes, filter the warm solution quickly (best with filter pump), and wash with water of about the temperature of 65°. Transfer the filter and its contents to a capsule, ignite until the organic matter is destroyed, treat with 10 to 15 c.c. of concentrated hydrochloric or nitric acid, digest over a low flame until the phosphate is dissolved, dilute to 200 c.c., mix, pass through a dry filter, take an aliquot and determine phosphoric acid as under total.

In case a determination of citrate-insoluble phosphoric acid is required in non-acidulated goods, it is to be made by treating 2 grms. of the phosphatic material, without previous washing with water, precisely in the way above described, except that in case the substance contains much animal matter (bone, fish, &c.), the residue insoluble in ammonium citrate is to be treated by one of the processes described below.

5. *Total Phosphoric Acid*.—Weigh 2 grms. and treat by one of the following methods:—(1) Evaporation with 5 c.c. magnesium nitrate, ignition, and solution in acid. This method is to be used in case of all fertilisers containing cotton-seed meal. (2) Solution in 30 c.c. concentrated nitric acid with a small quantity of hydrochloric acid. (3) Add 30 c.c. concentrated hydrochloric acid, heat, and add cautiously in small quantities at a time about 0.5 grm. of finely pulverised potassium chlorate.

Boil gently until all phosphates are dissolved and all organic matter destroyed; dilute to 200 c.c.; mix and pass through a dry filter; take 50 c.c. of filtrate; neutralise with ammonia (in case hydrochloric acid has been used as a solvent add about 15 grms. dry ammonium nitrate or its equivalent). To the hot solution for every decigram. of P_2O_5 that is present, add 50 c.c. of molybdic solution. Digest at about 65° C. for one hour, filter, and wash with water or ammonium nitrate solution. (Test the filtrate by renewed digestion and addition of more molybdic solution). Dissolve the precipitate on the filter with ammonia and hot water, and wash into a beaker to a bulk of not more than 100 c.c. Nearly neutralise with hydrochloric acid, cool, and add magnesia mixture from a burette; add slowly (one drop per second), stirring vigorously. After fifteen minutes add 30 c.c. of ammonia solution of density 0.95. Let stand several hours (two hours is usually enough). Filter, wash with dilute ammonia, ignite intensely for ten minutes, and weigh.

6. *Citrate-soluble Phosphoric Acid*.—The sum of the water-soluble and citric-insoluble subtracted from the total gives the citrate soluble.

Preparation of Reagents.

1. *To prepare Ammonium Citrate Solution*.—Mix 370 grms. of commercial citric acid with 1500 c.c. of water;

nearly neutralise with crushed commercial carbonate of ammonia; heat to expel the carbonic acid, cool, add ammonia until exactly neutral (testing by saturated alcoholic solution of coralline) and bring to volume of two litres. Test the specific gravity, which should be 1.09 at 20° C., before using.

2. *To prepare Molybdic Solution*.—Dissolve 100 grms. of molybdic acid in 400 grms. or 417 c.c. of ammonia of specific gravity 0.96, and pour the solution thus obtained into 1500 grms. or 1250 c.c. of nitric acid of specific gravity 1.20. Keep the mixture in a warm place for several days, or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phosphomolybdate. Decant the solution from any sediment, and preserve in glass stoppered vessels.

3. *To prepare Ammonium Nitrate Solution*.—Dissolve 200 grms. of commercial ammonium nitrate in water and bring to a volume of 2 litres.

4. *To prepare Magnesia Mixture*.—Dissolve 22 grms. of recently ignited calcined magnesia in dilute hydrochloric acid, avoiding excess of the latter. Add a little calcined magnesia in excess, and boil a few minutes to precipitate iron, alumina, and phosphoric acid, filter, add 280 grms. of ammonium chloride, 700 c.c. of ammonia of specific gravity 0.96, and water enough to make the volume of 2 litres. Instead of the solution of 22 grms. of calcined magnesia, 110 grms. of crystallised magnesium chloride ($MgCl_2 + 6H_2O$) may be used.

5. *Dilute Ammonia for Washing*.—One volume ammonia of specific gravity 0.96 mixed with three volumes of water, or usually one volume of concentrated ammonia with six volumes of water.

6. *Nitrate of Magnesia*.—Dissolve 320 grms. of calcined magnesia in nitric acid, avoiding an excess of the latter; then add a little calcined magnesia in excess, boil, filter from excess of magnesia, ferric oxide, &c., and bring to volume of 2 litres.

NOTICES OF BOOKS.

The Jeweller's Assistant in the Art of Working in Gold. A Practical Treatise for Masters and Workmen. Compiled from the Experience of nearly Thirty Years' Workshop Practice. By GEORGE E. GEE, Goldsmith and Silversmith, Author of "The Goldsmiths' Handbook," "The Silversmiths' Handbook," "The Hall-marking of Jewellery," &c., &c. London: Crosby Lockwood and Son.

MESSRS. LOCKWOOD AND SON are coming well to the front in the literature of metallurgy.

The present work is of a thoroughly practical character, and will, we feel convinced, be found exceedingly useful by the class to whom it is especially addressed; that is, not so much "beginners and young students, but advanced workmen of every department, as well as their employers." The author does not seek to enable his readers to talk about working in gold, but to practise with success.

To what extent rule of thumb holds sway even in the delicate art of the gold-worker may be judged from an incident narrated on pp. 17 and 18. We cannot help fearing that the master jeweller who figures there is the type of a class too numerous in all the arts. The country in which such characters are most numerous and most obstinate is precisely the one which will take the lowest rank in the industries of the future.

The work treats in successive chapters of the chemical and physical properties of gold, of the precipitation of gold in waste solutions, of the different colours of gold, of mixing and melting gold, of dry-colouring and wet-colouring gold, melting and casting gold, electro-gilding, other modes of gilding, practical manipulations, mixing alloys, useful imitation alloys, hints and helps, collecting

and refining, sundry gold alloys, choice recipes, and gold values and alloys.

Anyone who doubts whether this work was needed will be edified by reading certain passages in Chapter V. on "defective and wrong information," and "erroneous statements." In some departments a judicious well-read compiler may produce a useful treatise, but this is not the case in technology.

An Appeal to the Canadian Institute on the Rectification of Parliament. By SANDFORD FLEMING, C.M.G., LL.D., &c. Toronto: The Copp, Clark Company, Limited, 1892.

WHATEVER may be the views of the Canadian Institute, we, at any rate, must dismiss Mr. Sandford Fleming's "appeal" as being distinctly outside our jurisdiction.

Annual Archaeological Report and Canadian Institute (Session 1891): being an Appendix to the Report of the Minister of Education, Ontario. Printed by order of the Legislative Assembly. Toronto: Warwick and Sons, 1891.

This report is certainly scientific, and so far highly interesting, but it is entirely confined to archaeology, anthropology, and ethnology. The introduction is well worth reading.

A Systematic Course of Qualitative Chemical Analysis of Inorganic Substances. With Tests for the more important Metals and Acids. (For the Use of Students of Analytical Chemistry). Compiled by C. F. JURITZ, M.A., Fellow of the University of the Cape of Good Hope, Analytical Chemist; Senior Analyst, Department of Agriculture, Cape Colony. Cape Town and Johannesburg: J. C. Jutta and Co.

THIS "systematic course" is compact and correct in its indications, but we can scarcely enter into the author's views when he writes in his preface: "In default of the existence of a suitable course of qualitative analysis in the English language, I found it necessary while a student at the South African College to translate for my own use, from the German, certain portions of the late Professor Heintz's work on qualitative analytical chemistry." We should have thought the only difficulty would be to make a selection of any one book out of so many, all correct in their teachings, and which earned the approval of the profession. For us to recommend any one manual out of the crowd would be scarcely just either to the authors or to the publishers of the others.

We wish Mr. Juritz could have seen his way to use the nomenclature adopted by the Chemical Society.

Development of Gases.—Neumann (*Journ. fur Prakt. Chemie*).—The author obtains continuous currents of hydrochloric acid gas from carnallite and concentrated sulphuric acid; gaseous ammonia from solid potassium hydroxide and aqueous ammonia; nitrogen from chloride of lime and ammonia.

Methods Proposed for Determining Paratoluidine in Commercial Toluidines.—F. F. Raabe (*Chemiker Zeitung*).—After criticising previous methods the author lays down the following process, by means of which he has obtained good and expeditious results. He adds to a commercial sample so much weighed paratoluidine as to yield a mixture the congealing-point of which can be determined. A thermometer with a scale extending from 30°—50°, and graduated in twentieths of a degree, shows differences of 0.2 per cent of paratoluidine. As standards he prepares solutions containing, respectively, 82.5, 83, 83.5, 84, 84.5, and 85 paratoluidine, and determines their congealing-points. It is recommended always to work with equal quantities. The toluidines to be used in this determination must be anhydrous.

CORRESPONDENCE.

WANTED,—CONSISTENCY.

To the Editor of the Chemical News.

SIR,—It is with regret that I see that your correspondent "Ous" thinks me wanting in consistency in using the terms sodic and magnesian sulphates. As I can hardly make out from his letter whether he approves of my nomenclature or not, I had better reply by stating my reasons for using the terms.

I regard the words sodic and magnesian as adjectives. Just as the name acid of sulphur was changed into sulphuric acid, so chloride of sodium has been altered into sodic chloride, or that chloride which is sodic. The name sodium chloride seems to me incorrect, and not analogous to the German chlornatrium. Up to the present (happily or unhappily?) we do not construct compound substantives, or we should translate chlornatrium into chlorine sodium or sodium chlorine, and certainly not sodium chloride.

If sodic chloride is inadmissible,—so must of necessity be hydrochloric acid,—"Ous" would probably take refuge in the name hydrogen chloride. On one point, however, I think we should agree, namely, in condemning the use of loose expressions that we sometimes hear from students, such as "dissolving a substance in hydrochloric."

I do not think that the terms sodic and magnesian sulphates at all imply the existence of sodious and magnesian compounds. An equal objection might be taken to my using the expressions "an enormous house" or "a terrific storm," as necessarily implying "an enormic house" or a "terrific" or "perterrific" storm.—I am, &c.,

HERBERT MCLEOD.

Scarborough, Aug. 22, 1892.

A CURIOUS POINT IN THE HISTORY OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—One of my friends, who is the owner of a bound copy of the CHEMICAL NEWS for the year 1868, was good enough to allow me to refer to the report of the Anniversary Meeting of the Chemical Society, held March 30, 1868, and in your report I find the missing list of officers and council elected at the meeting.

As I mentioned, there is a curious interest attached to that list, and the circumstance that it is to be found in your pages and not in the volume of the *Journal of the Chemical Society* is very singular. The omission forms one of a series.

On June 18, 1868, I read a paper to the Chemical Society, the title of which is to be found in the Society's Journal, but the paper itself will be sought for in vain in its pages. An abstract of it, and also a curious discussion on the paper, is to be met with in the CHEMICAL NEWS.—I am, &c.,

J. ALFRED WANKLYN.

New Malden, Surrey,
Aug. 23, 1892.

ESTIMATION OF CAOUTCHOUC.

To the Editor of the Chemical News.

SIR,—With regard to the remarks made by your correspondent Mr. Carter Bell in the CHEMICAL NEWS (vol. lxvi., p. 84), I may say that there was no "rubber substitute" present in the rubber mat in question. Although I will admit that the presence of old rubber is very probable, as suggested by your correspondent Mr. J. K.

Burridge at page 97. A good price was paid for the mat, and it is well known that mats are made with pure caoutchouc mixed with old rubber, the total caoutchouc in the composition amounting to over 50 per cent. The following is an analysis of such a mat as made by M. Guibal:—

Caoutchouc	40	} = 55 per cent.
Chippings of vulcanised rubber	15	
Litharge	35	
Chalk	8	
Sulphur	2	
	100	

The writer is at present engaged in research work on rubber and gutta-percha goods, and hopes to be able to publish results later on.

Apropos of gutta-percha, I recently had a sample of gutta-percha dielectric submitted to me for analysis, supplied to specification as "best gutta-percha." From this sample I succeeded in dissolving out by boiling absolute alcohol 47 per cent of resin. According to M. Payen, ordinary gutta-percha should not give up more than 22 per cent of resinous matter to boiling alcohol—this amount, of course, being naturally present in the substance. From a sample of raw gutta-percha obtained from a leading firm of manufacturers in London I extracted 30 per cent of resinous matter. No doubt the amount soluble in alcohol varies in samples obtained from different countries.

I should be pleased to hear from any chemist who has estimated the maximum proportion of resin, &c., dissolved by raw gutta-percha obtained from various sources.—I am, &c.,

H. JOSHUA PHILLIPS, F.I.C.

G.E.Ry. Laboratory, Stratford,
London, August 22, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 11.

The Determination of Nitrogen in Nitrates, Nitric Ethers, and Nitro-Derivatives, by Kjeldahl's Method.—L. Chenel.—The author's analytical results prove that Kjeldahl's method with Jodibauer's modification facilitates the analysis of many compounds which require the method of Dumas. As it consists of an interrupted series of three or four very simple operations, it has the advantage over the Dumas process of being less burdensome, and of not requiring a prolonged and sustained attention.

New Derivatives of Amethylcamphonitroketone.—P. Cazeneuve.—Already inserted.

Tinctorial Properties of Methylcamphonitroketone and its Auxochromic Grouping.—P. Cazeneuve.—Already inserted.

New Bacillus found in Rain-Water.—Dr. A. B. Griffiths.—Already inserted.

The Preservation of Solutions of Sulphuretted Hydrogen.—MM. Salazar and Neumann.—The authors draw from their experiments the conclusions that solutions of H₂S keep better the smaller the quantity of air to which they are exposed. As regards preservation there is great advantage in dissolving the H₂S in Lepage's mixture in preference to water. The oxidation of dissolved H₂S is more rapid in light than in darkness.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xix., No. 1.

The Principles of Modern Agriculture.—J. Pyro.—The author admits that certain plants are capable of fixing atmospheric nitrogen. He quotes Paliass as having many years ago insisted on the restoration to the soil of all the waste products of vegetable and animal life. He criticises Ville's "sideration" as having been long known and practised, forgetting that at present a vast part of the solar energy which actually reaches our earth is allowed to be wasted.

Volumetric Determination of Mercury.—M. Rod. Namias (*Gazzetta Chimica Italiana*).—This paper will be inserted in full.

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PRINCIPAL—PROF. R. S. HEATH, M.A., D.Sc.

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The SESSION 1892-93 will be opened on FRIDAY, SEPTEMBER 30, 1892, by Prof. SIR GEORGE HUMPHRY, M.D., F.R.S., F.R.C.S., who will distribute the Prizes and deliver an Address.

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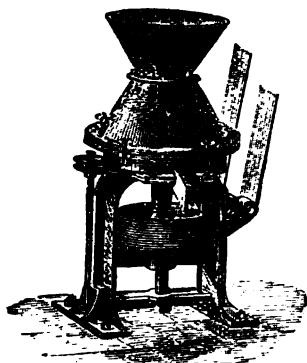
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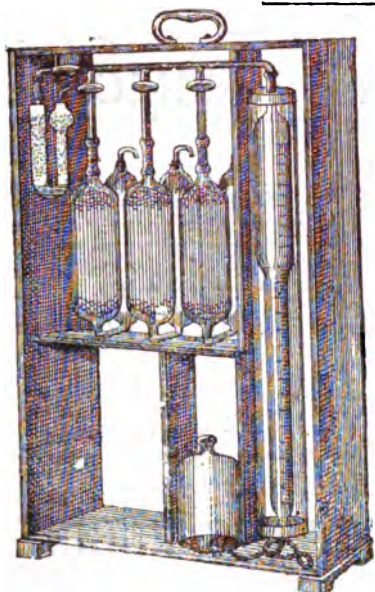
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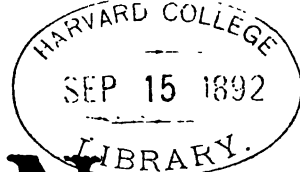
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The NEW SESSION commences on September 28th.

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NOTICE.

The STUDENTS' NUMBER of the CHEMICAL NEWS will be published on Friday, September 9th. Gentlemen holding official positions in the Universities, Medical Schools, &c., of the United Kingdom, where Chemistry and Physical Science form a part of the education, who have not yet forwarded the necessary information to our Office for publication in that Number, will confer a favour by sending it with the least possible delay.

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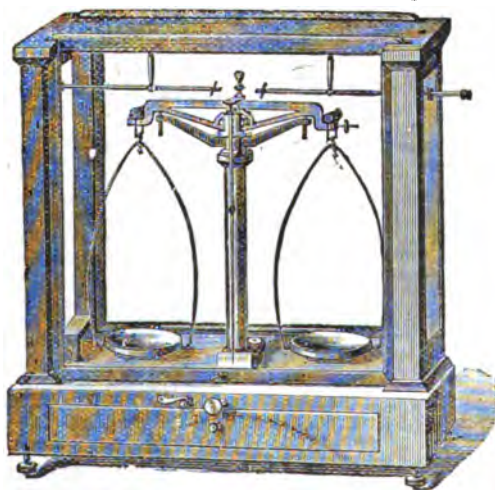


FIG. 3A.

SHORT BEAM BALANCE, Fig. 3A, No. 12A, to carry 2000
grains in each pan, sensible to 1-300th grain. Agate bear-
ings, one rider apparatus. Nickel pans, 3 in. diameter... £7 6 0
Same, with agate knife edges £8 6 0
Same with supports for pans, extra £1 0 0
ANALYTICAL BALANCE, No. 12, to carry 100 grammes
in each Pan, sensible to 1-5th milligramme. Agate bear-
ings. Nickel Pans 3 in. diameter £7 1 8
Same, with agate knife edges £8 1 8
Same with supports for pans, extra £1 0 0
STUDENTS' BALANCE, in Polished Mahogany Glass
Case, to carry 30 grammes and turn to $\frac{1}{4}$ milligramme £2 10 0
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THE CHEMICAL NEWS.

Vol. LXVI., No. 1710.

ON THE IODIDES OF SULPHUR.*

By Prof. HERBERT McLEOD, F.R.S.

AN iodide of sulphur, SI_6 , isomorphous with iodine, was prepared by Landolt and measured crystallographically by Vom Rath (*Poggendorff's Annalen*, cx., 116). It was made by allowing a solution of iodine and sulphur in carbonic disulphide to evaporate spontaneously. As the existence of this compound has been adduced as a proof of the hexad character of sulphur, it seemed advisable to investigate its properties.

Some of the substance was prepared by the process mentioned, and in order to separate it from any admixture of iodine, it was placed in a tube which was afterwards exhausted by the Sprengel pump and sealed. One end of the tube was then surrounded by muslin kept wet with water by means of a piece of cotton wick; iodine volatilised, at first rapidly but afterwards more slowly. After the lapse of three months a residue was left at the end of the tube which, on analysis, was found to contain 98.5 per cent of sulphur.

Another quantity was dissolved in carbon disulphide and the solution allowed to evaporate; as crystals were formed the liquid was poured off and the crystals washed with carbonic disulphide. In this manner five crops of crystals were obtained, none of which contained more than half a per cent of sulphur; the residue left on allowing the mother-liquor to evaporate contained 56 per cent of sulphur.

The iodine is entirely removed from the substance by digesting it in a solution of potassic iodide.

When some of the powdered substance is exposed to the air in a shallow layer, the iodine all volatilises, leaving a residue of sulphur.

When acted on by a solution of sodic hydrate, a residue of sulphur is left, and the solution gives very little precipitate with baric chloride after acidifying with hydrochloric acid.

The properties of the substance seem to indicate that it is a mechanical mixture of iodine and sulphur and not a chemical compound.

Some experiments were then made with the iodide of sulphur, S_2I_2 , described by Guthrie. This was prepared by mixing chloride of sulphur, S_2Cl_2 , with ethylic iodide, and allowing the mixture to remain in a sealed tube for four days. Black crystals were then found in the tube. On opening the latter a large quantity of the vapour of ethylic chloride escaped.

The crystals were removed from the tube and powdered. On heating a portion in a test-tube it fused at a temperature a little above the boiling-point of water.

Some of the substance *in vacuo* gave off iodine, leaving a light coloured residue. Some of the substance dissolved in sulphide of carbon was crystallised fractionally; the first crop contained 0.38 per cent of sulphur; the second 0.31; the third 1.07; and the fourth 34.78. On allowing the mother-liquor to evaporate, the residue contained 76.32 per cent of sulphur.

When acted on by a solution of sodic hydrate the iodine is removed and all the sulphur remains behind, the solution giving no precipitate with baric chloride after adding hydrochloric acid. It is usually stated in text-books that the compound undergoes a decomposition similar to that of the chloride of sulphur, forming an iodide and a sulphite or thiosulphate, with separation of sulphur.

* Read before the British Association, Edinburgh Meeting, 1892, Section B.

The fusing-point being lower than those of iodine and sulphur would indicate that some chemical action takes place when the elements are mixed together, but its properties more resemble those of a non-metallic alloy than of a definite chemical compound.

THE HALOGEN ADDITION PRODUCTS OF SALTS OF ORGANIC BASES.*

By LEONARD DOBBIN, Ph.D., and JAMES WALKER, Ph.D., D.Sc.

DOBBIN and Masson prepared well-defined compounds, NMe_4IBr_2 , NMe_4ICl_2 , SM_2IBr_2 , and SM_2ICl_2 , by the action of bromine and of chlorine on the iodides of tetramethylammonium and of trimethylsulphine. The authors have now prepared analogous compounds, $(C_5H_5N)CH_3IBr_2$ (m.p. 63°) and—

$(C_5H_5N)CH_3ICl_2$ (m.p. 88°),

from methylpyridium iodide. These trihalogen compounds are not equally stable on exposure to moist air, the dibromiodides being more stable than the dichloriodides, and the methylpyridium derivatives being much more stable than the corresponding trimethylsulphine derivatives, with the tetramethylammonium compounds in an intermediate position. In order to test their stability with regard to boiling alcohol, determinations of the elevation of the boiling-point of their alcoholic solutions were made by means of Beckmann's apparatus, and from these observations the molecular weights were calculated with the following results:—

	Dibromiodides.		Dichloriodides.	
	Theory.	Found.	Theory.	Found.
Methylpyridium . . .	381	386	292	276
Tetramethylammonium . .	361	353	272	239
Trimethylsulphine . . .	358	293	269	208

These numbers show that the dibromiodides of methylpyridium and tetramethylammonium are not appreciably attacked by boiling alcohol; that methylpyridium dichloriodide is slightly attacked; and that the other compounds are all decomposed to a marked extent by five to fifteen minutes' boiling. If the boiling is prolonged the molecular weights of the dichloriodides sink continually, indicating increased decomposition, which may also be observed from the change of colour of the solutions. There is thus a continuous series of analogous compounds ranging from methylpyridium dibromiodide, which is perfectly stable in boiling alcohol, down to trimethylsulphine trichloriodide, which is at once decomposed by cold alcohol, being only stable in an atmosphere of dry chlorine. The first mentioned substance has all the characters of an ordinary "atomic compound"; the second those of a so-called "molecular compound"; yet these substances are only the extreme terms of a continuous and perfectly uniform series, so that atomic and molecular compounds must be of the same order.

WATER ANALYSIS.

(No. II.)

By J. ALFRED WANKLYN.

ALTHOUGH the first detailed and authoritative publication of Frankland's "Water Analysis" took place in the *Journal of the Chemical Society* for the year 1868, the essential features of the process were disclosed before the advent of Wanklyn, Chapman, and Smith's ammonia-process; and it is historically true that our process was

* Read before the British Association, Edinburgh Meeting, 1892, Section B.

produced under a lively sense of the great difficulty and utter futility of the Frankland process. Both Chapman and myself had had personal experience of the working of one of the initial forms of Frankland's process, and that experience formed an important factor in determining the nature of the ammonia-process. Not only did we recognise that it was absolutely impossible for Frankland's method to measure the carbon and nitrogen existing in drinking waters, but we went much further and opened our eyes so as to see that a knowledge of the total organic carbon and nitrogen in drinking water would not supply the datum required for sanitary purposes.

It is only right to remark that the belief in the necessary inutility of the organic carbon and nitrogen determination was by no means confined to Chapman and myself, but was shared by leading authorities a quarter of a century ago; and that very careful and trustworthy chemist, Dr. William Allen Miller, expressed himself very strongly as to the uselessness of such determinations. A consideration which led chemists of a former generation to decline to attempt a Frankland measurement of organic carbon was that such a measurement (even if valid), would lump together the end products of vegetable and animal disintegration with the fresh intact vegetable and animal products. The general vegetable products, cellulose, starch, sugar, and gluten, enter into many drinking waters and presently ferment, yielding carbonates, nitrates, acetates, lactates, succinates, and other products. Now traces of acetates, lactates, benzoates, succinates, and traces of hydrocarbons, are neither harmful nor indicative of danger, and a total organic carbon determination would register them as if they were dangerous.

In striking out a new line of water analysis we resolved not to lump together all the organic matter,—not to confound that which was harmless and not indicative of danger with that which was either harmful or indicative of danger. We reflected that the harmful or dangerous organic matter must be either itself albuminous or else a complex nitrogenous derivative of albumen. Water destitute of such materials would be perfectly safe; water containing much of such materials we recognised as either harmful or risky.

Our measurement of albuminous substances, whether of animal or vegetable origin, was founded on the observation that egg albumen or gluten yields about one-tenth of its weight of ammonia when operated upon under certain sharply defined conditions. Ammonia obtained from a drinking water under these conditions I named albumenoid ammonia. The quantity of ammonia obtained under these conditions is the measure of the albuminous substance in the water. It is the measure of the potential albumen. If all the complex nitrogenous organic matter consisted of egg albumen or gluten the actual weight of it would be ten times the weight of the albumenoid ammonia; if it existed in other states of combination other weights of nitrogenous substance would correspond to a given weight of albumenoid ammonia. There is no reason to expect that the real absolute weights of the dry nitrogenous substances would be at all a better numerical expression for the degree of contamination than the quantities of albumenoid ammonia directly measured and recorded.

In the whole history of chemical analysis there is hardly any process which has been subjected to more rigid practical investigation. It is now twenty-five years old, and its appreciation has had no other source than its own trustworthiness and especial adaption to the purposes for which it was designed. How many persons at present employ our process in different parts of the world is to be reckoned at many thousands, and nearly ten thousand copies of our work on water analysis are in the hands of the public. Under these circumstances any endeavour to suppress the ammonia-process is likely to prove as futile as an attempt to stop the rising tides. But we are threatened

with a visitation of cholera, and the perverse action of a Government department might for the moment deprive the nation of the advantage of a correct discrimination of the different kinds of drinking water, which at times like the present means life or death to individuals.

Whether or not there is risk that a given well is cholera laden is a question to which the ammonia-process can give a correct answer; it remains to be seen whether the opportunity will be given to that process.

New Malden, Surrey,
Aug. 30, 1892.

METHODS OF ANALYSIS OF FERMENTED LIQUORS.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

I. *Specific Gravity*.—This determination is made with a pycnometer, or a Westphal balance controlled by a pycnometer. Temperature 25° C.

II. *Alcohol*.—One hundred c.c. of wine at 25° C. distilled (preferably in glass) give + c.c. alcohol.

III. *Extract*.—Fifty c.c. of wine (at 25° C.), in case of sweet wines a less amount, are evaporated in a platinum dish on the water-bath to the proper consistency, and then dried in a drying oven at 100° C. to constant loss of weight. Constant loss of weight is assumed when three weighings with equal intervals between the first and second and second and third give equal differences between the successive weighings. Weighings are to be made at intervals of fifteen minutes.

(*Note on the Extract Determination*.—So far as I am aware no satisfactory method has been given for the determination of the extract of wine. I think that the method of the Bavarian chemists is on the whole the best. As the object is for purpose of comparison with some standard, we cannot do better, I think, than to follow the standard most generally adopted. I have in mind when the new Chemical Laboratory of the University of California is fitted up to make some experiments on the determination of this extract in a vacuum at a moderate temperature. I should modify somewhat the method of Gautier. However, until some better method has been established, I believe the method given will be most satisfactory).

IV. *Acidity* (total acid constituents of the wine expressed as tartaric acid).—If carbonic acid is present, expel by shaking. Titrate with dilute alkali solution. The neutral point is determined by adding a drop of solution to delicate litmus-paper.

V. *Volatile Acids* (expressed as acetic acid).—Distil in a current of steam, and titrate the carefully condensed distillate with standard alkali (decinormal).

VI. *Glycerin*.—(1) This is determined in dry wines as follows:—The alcohol is driven off from 100 c.c. wine, lime or magnesia added, and the same evaporated to dryness. The residue is boiled with 90 per cent alcohol, filtered, and the filtrate evaporated to dryness. This residue is dissolved in 10 to 20 c.c. alcohol, 15 to 30 c.c. ether added, and the mixture allowed to stand until it is clear. It is then decanted from the sticky precipitate into a glass-stoppered weighing bottle, evaporated to constant loss of weight, and weighed.

(2) The following method is employed for sweet wines:—One hundred c.c. wine are measured into a porcelain dish and evaporated on the water-bath to a syrupy consistence, mixed with 100 to 150 c.c. absolute alcohol, poured into a flask, ether added in the proportion of 1½ volumes to each volume of alcohol used, the flask well shaken, and allowed to stand until the liquid becomes clear. This is then poured off, and the residue again treated with a mixture of alcohol and ether. The liquids are mixed, the alcohol and ether driven off, the residue dissolved in water, and treated as in (1).

(3) In all glycerin determinations it is necessary to take into consideration the loss of glycerin due to its volatility with water and alcohol vapour, and accordingly to add to the glycerin found 0.100 grm. for each 100 c.c. of liquid evaporated.

(4) It is necessary to test the glycerin from sweet wines for sugar, and if any is present it must be estimated by Sohlet's or Knapp's method, and its weight subtracted from that of the glycerin.

VII. *Sugar*.—This is to be determined by Sohlet's or Knapp's method. The presence of unfermented cane-sugar is to be shown by inversion, &c.

Polarisation.—(1) The wine is decolourised with plumbic subacetate.

(2) A slight excess of sodic carbonate is added to the filtrate from (1). 2 c.c. of a solution of plumbic subacetate are added to 40 c.c. white wine, and 5 c.c. to 40 c.c. red wine; the solution is filtered, and 1 c.c. of a saturated solution of sodic carbonate added to 21.0 or 22.5 c.c. of the filtrate.

(3) The kind of apparatus used and the length of the tube are to be given, and results estimated in equivalents of Wild's polaristrobometer with 200 m.m. tubes.

(4) All samples rotating more than 0.5 degree to the right (in 220 m.m. tubes, after treating as above), and showing no change, or but little change, in their rotatory power after inversion, are to be considered as containing unfermented glucose (starch sugar) residue.

(5) Rotatory power of less than 0.3 degree to the right shows that impure glucose has not been added.

(6) Wines rotating between 0.3 degree and 0.5 degree to the right must be treated by the alcohol method.

(7) Wines rotating strongly to the left must be fermented, and their optical properties then examined.

VIII. *Tannin*.—Determine with Neubauer's permanganate method.

IX. *Potassic Bitartrate*.—The determination of potassic bitartrate as such is to be omitted.

X. *Tartaric, Malic, and Succinic Acids*.—(1) According to Schmidt and Hiepe's method.

(2) Determination of tartaric acid according to the modified Berthelot-Fleury method.

(3) If the addition of 1 grm. finely powdered tartaric acid to 100 grms. wine produces no precipitate of potassic bitartrate, the modified Berthelot-Fleury method must be employed to determine free tartaric acid.

XI. *Colouring Matter*.—(1) Only aniline dyes are to be looked for.

(2) Special attention is to be paid to the spectroscopic behaviour of rosaniline dyes as obtained by shaking wines with amylic alcohol before and after saturation with ammonia.

XII. *Inorganic Matter* (ash).—Burn in ordinary manner in flat platinum dish at as low a heat as possible; repeated moistening, drying, and heating to redness are advisable to get rid of all organic substances.

XIII. *Citric Acid*.—Presence to be shown by a qualitative test, as baric citrate.

XIV. *Sulphuric Acid*.—To be determined in the wine after adding hydrochloric acid.

XV. *Chlorine*.—To be determined in the nitric acid solution of the burnt residue by Volhard's method.

XVI. *Lime, Magnesia, and Phosphoric Acid*.—These are determined in the ash fused with sodic hydrate and potassic nitrate, the phosphoric acid by the molybdenum method.

XVII. *Potash*.—Either in the wine ash, as the platinum double salt, or in the wine itself, by Kayser's method.

XVIII. *Gums*.—Presence shown by precipitation by alcohol; 4 c.c. wine and 10 c.c. 96 per cent alcohol are mixed. If gum arabic has been added, a lumpy, thick, stringy precipitate is produced; whereas pure wine becomes at first opalescent and then flocculent.

XIX. *Sulphurous Acid*.—One hundred c.c. of wine are distilled in a current of carbonic acid after the addition of phosphoric acid. The distillate carefully condensed is

oxidised with bromine, and the amount of H_2SO_4 determined.

Abnormal Constituents of Wines.

Mannite.—When present in any considerable quantity it can be detected by simply allowing the wine (a few drops will be sufficient) to evaporate spontaneously upon a glass slide or plate. The mannite will crystallise in a characteristic stellated form, which can be recognised at a glance. It should be allowed to stand twenty-four to forty-eight hours. When the quantity is small, extract the residue evaporated nearly or quite to dryness with boiling 80 per cent alcohol. Evaporate this extract to dryness, and extract with 95 per cent boiling alcohol; the mannite, if present in any quantity, will separate out in part upon cooling. If allowed to evaporate spontaneously the characteristic stellated crystals can be obtained.

Lactic Acid.—This will be found in the alcohol ether extract of evaporated residue, and can be recognised by usual tests. It may be determined by titration with standard alkali. It may be necessary to take larger quantities of the wine for this investigation.

In diseased wines butyric acid may be tested for in the portion of volatile acid.

A QUICK METHOD OF PREPARING SILICON, ALUMINIUM, AND OTHER CHLORIDES IN QUANTITY.

By H. N. WARREN, Research Analyst.

For the preparation of silicon chloride a sample of silicon-eisen containing about 15 per cent silicon was selected, introduced into a deep clay retort provided with a tubulure, and connected with an apparatus evolving dry chlorine gas, the pipe conveying the gas passing nearly to the bottom of the retort, while the stem of the same was connected to a suitable adapter, maintained at the required heat by the aid of hot water, and intended to condense and retain the volatile ferric chloride, which would naturally accompany the silicon chloride; the termination of the adapter being further connected with a suitable refrigerator containing a mixture of salt and ice in order to retain the volatile tetrachloride of silicon, SiCl_4 .

The retort and its contents being now raised to redness by the aid of ignited charcoal, and the chlorine then allowed to play into the same, almost immediately the dense greenish yellow vapour of gaseous ferric chloride is observed traversing the space within the adapter, and speedily condensing into the form of brilliant plates upon the walls of the same; while, at the more remote end, is observed the condensation of the silicon chloride, not unfrequently contaminated by the presence of small quantities of ferric chloride, which, however, may be entirely removed by subjecting the latter to distillation.

Further advantages may be obtained by substituting for the chlorine gaseous hydric chloride. This gas, on account of its forming with the iron a ferrous salt, practically non-volatile at ordinary temperatures, is itself retained in the retort, and at the termination of the reaction may be detached by pouring the same while in the liquid form, while, at the same time, a further charge may be introduced. Thus, by acting upon the element silicon at an elevated temperature by means of gaseous hydric chloride, a still more volatile liquid chloride of silicon is obtainable, corresponding to a hydro-trichloride, and represented by the formula of SiHCl_3 . In this instance, however, the formation of silicon itself, which in the elementary form is by no means easy as regards its preparation, is absolutely necessary; but, by substituting for the same a sample of silicon-eisen containing a rich percentage of silicon, the corresponding chloride may be as readily prepared as in the former instance.

For the preparation of aluminium chloride an alloy of

iron and aluminium containing about 10 per cent of the latter was selected, and the chloride thus obtained purified by intimately mixing it with iron borings and distilling the same; or the pulverised regulus mixed with common salt previous to exposing it to the action of chlorine yields as a sublimate aluminium-sodium-chloride.

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ON THE DISSOCIATION OF ELECTROLYTES IN SOLUTION AS SHOWN BY COLORIMETRIC DETERMINATIONS.

By H. M. VERNON, B.A.

(Continued from p. 105).

POTASSIUM chromate and bichromate solutions show no irregularities like those of the chromic salts. Potassium chromate solution does not appear to decrease in colour in the least even at 100 litres dilution. Chromic oxide, on the other hand, shows great decrease, the colour effect at 100 litres being less than half that of the normal solution. This is probably owing to the colour of the concentrated solution, being in great part due to the presence of excess of chromium trioxide molecules dissolved in the H_2CrO_4 existing in solution, and which as dilution proceeds, are gradually converted into H_2CrO_4 , with decrease of colour effect of the solution. Thus it is known that when sulphuric acid is added to a solution of potassium bichromate it becomes considerably darkened in colour, and this can only be due to the presence of chromium trioxide existing as such in the solution. If the colour produced by viewing solutions of potassium chromate and chromium trioxide in separate tubes, placed one on top of the other, be compared with the colour of a solution of potassium bichromate of equivalent strength, it is found that the bichromate solution is more than four times as dark in colour. It is thus evident that potassium bichromate, even in solution, forms a distinct and stable compound, and does not decompose into K_2CrO_4 and CrO_3 .

Ferric chloride solutions gave peculiar results. This was due to the presence, in the ferric chloride solutions, of free iron sesquioxide, the formation of which was probably due rather to the action of the mass of water present than to the electrolytic dissociation of the ferric chloride.

The acid ferric chloride solutions contained six equivalents of free hydrochloric acid to the normal and 5 litre solutions, and twelve equivalents to the 10 and 100 litre solutions. It was not possible to colorimetrically compare the 1 and 5 litre solutions, as the 1 litre solution was a yellowish brown colour, and the 5 litre solution a bright yellow. The acid ferric chloride solution is remarkable in that it shows a far greater colour decrease on dilution than any other salt examined. In solution ferric chloride is evidently an unstable salt, both in the ordinary sense of the word and in the electrolytic dissociation sense.

Ferric acetate proved to be a very unstable salt when no free acetic acid was present, it decomposing spontaneously with precipitation of the basic acetate. 2 c.c. of free acetic acid was therefore added to 100 c.c. of the solution. Like ferric chloride, the solution increases in colour effect on dilution, and, as will be shown later, probably from the same reason. A stronger solution than the decinormal could not be examined, as it was so dark in colour. The two separate series of determinations made with solutions of ferric citrate, and of ferric citrate containing five molecules of free citric acid, showed no difference in dissociation values, but both showed great increase of colour on dilution. Ferric citrate free from

citric acid was obtained by decomposing barium citrate with ferric sulphate.

Ferric oxalate solution was prepared by boiling precipitated ferric oxalate with oxalic acid solution till no more would dissolve and filtering off the solution. In its behaviour on dilution the solution of this salt resembles acid ferric chloride solution, though it does not dissociate to so great an extent. Ferric ammonium citrate solution behaves quite differently, however, and does not on dilution appear to change at all in colour effect. Ferric tartrate solution, containing no free tartaric acid, was prepared by decomposing barium tartrate with ferric sulphate. It showed a greater increase of colour effect on dilution than the solution of any other salt examined. This was due to the same cause that produced the great increase of colour effect with solutions of ferric chloride and acetate, i.e., the formation in solution of ferric oxide. The quantity of iron in these ferric salts was determined by evaporating down and igniting some of the salt in a platinum crucible, moistening with nitric acid, again igniting, and weighing as Fe_2O_3 .

Ferrous citrate solution was prepared by decomposing barium citrate with ferrous sulphate. It decreases greatly in colour effect on dilution.

Potassium ferrocyanide and ferricyanide solutions decrease in colour effect to a moderate extent on dilution, whilst potassium permanganate only shows traces of decrease at extreme dilutions. The values given for this salt are for solutions a hundred times more dilute than the dilutions they are placed under, for more concentrated solutions were too dark for colour comparison. The slight increase in colour effect at dilutions of 1000 litres and 10,000 litres are rather too great for experimental error.

The general conclusions to be drawn from the changes in colour attending the dilution of solutions of coloured salts are, that almost all salt solutions show a decrease in colour effect; but a few, notably several organic salts of iron, show a considerable increase in colour. It is difficult to find an adequate explanation for these changes in colour effect, except on the ground of electrolytic dissociation. Of the salts examined which do not decrease in colour effect on dilution, the chromium salts are the most notable instances. Potassium chromate was not, perhaps, examined at a sufficient dilution, for potassium permanganate, a salt to which it bears some sort of resemblance, only showed a decrease in colour effect at a dilution of 50,000 litres. The ferric salts are the chief exceptions, but the cause of such behaviour on the part of ferric chloride has already been explained. It is thus seen that with a few doubtful exceptions coloured salts, by the decrease in colour effect of their solutions on dilution, appear to undergo partial dissociation.

The reciprocals of these colour effect values for different salts should be proportional to their electrical conductivities at the same dilutions. Not many of the salts examined here appear to have been examined electrically, but as a general rule it is evident that the colour effects of salts do not decrease to so great an extent as the electrical conductivities increase. Thus most salts on dilution from 1 to 1000 litres have their conductivities more than doubled. It must be remembered, however, that it has not been shown whether or no the dissociated ions themselves produce any colour effect in a solution. From the fact that while most ferric salt solutions are deeply coloured, and that of the sulphate is nearly colourless, it does not seem to be essential that a base forming some salts coloured should form all. Also most ferrous salts form only slightly coloured solutions. Again, cupric sulphate in the anhydrous state is a white powder. On the other hand, in that all cupric, cobalt, nickel, chromium, and uranium salts form coloured solutions, it would seem that the formation of such coloured solutions is so essential a property of salts of certain metals that it cannot be considered impossible that this property should extend even to the ions, though it is far from probable. It is

not possible therefore to speak with certainty either way. The changes in colour effect of solutions of salts on dilution are evidently due to more than one cause. As will be shown, the formation of hydrates will account for them in part. They cannot be wholly accounted for in this way, however. Electrolytic dissociation seems to be the only ground left on which an explanation is possible.

(To be continued.)

NOTES UPON THE ESTIMATION OF CHLORINE IN ELECTROLYSED SOLUTIONS.

By L. M. NORTON, Ph.D.

THE numerous experiments made during the last few years upon the production of chlorine, hypochlorites, and chlorates by the electrolysis of solutions of chlorides, have brought into the hands of analysts solutions containing chlorine in several combinations.

It has been found that rapid volumetric methods for the determination of the combinations in which the chlorine existed were a necessity where such solutions were to be frequently tested, and the writer thinks a description of the methods he has employed, while they contain little that is new, may be of interest to chemists who deal with similar problems.

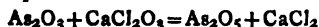
By the direct electrolysis of aqueous solutions containing sodium chloride at ordinary temperatures, solutions are obtained which contain sodium chloride, sodium hypochlorite, and sodium chlorate, and this general action is undoubtedly true in regard to other chlorides. A most careful examination has failed to show the presence of sodium chlorite in solutions thus prepared. If, however, the temperature is raised to 50–55° C. (Rigaut, "*La Lumière électrique*, xl., 102) the solution contains mainly sodium chloride and sodium chlorate.

Such solutions may be very conveniently examined by the methods described below.

Estimation of Chlorine combined as Hypochlorite.

A quantity, 25 c.c. for example, of the solution is measured out and titrated in the ordinary manner with a sodium arsenite solution of known strength. The solution after the titration must be preserved for the determination of the chloride present.

From the equation—



the quantity of chlorine combined as hypochlorite may be calculated.

Estimation of Chlorine combined as Chloride.

The portion of the original solution which has been titrated with sodium arsenite is now conveniently made up to a known volume and an aliquot part is taken. To this part a solution of pure potassium chromate is added, and the solution then titrated with silver nitrate of known strength. The presence of arsenic compounds does not interfere with this titration in any way; in fact, sodium arsenite may be used as an indicator in the place of potassium chromate, and equally good results may be thus obtained.

The figures furnished by the titration with silver solution give the chlorine present as chloride and hypochlorite together in the original liquid. By subtracting the chlorine combined as hypochlorite from the chlorine shown by the titration with silver solution, the chlorine present per c.c. as chloride is readily obtained.

Estimation of the Total Chlorine.

It might seem at first thought that the total chlorine could be obtained by the titration of the original solution which had been electrolysed; but this is not the case, a

during the electrolysis of a chloride solution there is a decrease in its volume caused by the rise in temperature due to the current, so that the contents per c.c. of the solution before and after electrolysis are not comparable, unless, in the latter case, the solution is carefully brought to its original volume by the addition of water. A further error is unavoidably introduced by a loss of chlorine due to its escape directly into the air during the electrolysis, a loss which the writer has always observed in the various forms of apparatus which he has used.

As the solutions under discussion contain chlorine in two oxidised forms, as well as in the form of chloride, it is of course evident that for the determination of the total chlorine the simplest method will be the reduction of the oxidised chlorine compounds to the form of chloride, and a subsequent titration with silver solution. Various reducing agents have been recommended from time to time for the reduction of chlorates to chlorides with a view to the subsequent titration of the chlorides with silver solution. After many experiments, the writer has found that the most satisfactory agent for this reduction is a saturated aqueous solution of sulphurous acid. This was suggested by Rose ("*Handbuch der Analytischen Chemie*," ii., 613, Leipzig, 1871), and lately Engel (Silva, "*Traité d'Analyse Chimique*," 151, Paris, 1891) has called attention to its possible use in this connection. Chlorates are completely reduced to chlorides by boiling for a few moments with an excess of an aqueous solution of sulphurous acid, with or without the addition of nitric or sulphuric acid. Thus the following figures were obtained in the analysis of a sample of commercial chlorate of potash by reduction with sulphurous acid solution, after acidifying strongly with nitric acid, boiling off the excess of sulphurous acid, followed by titration with silver solution in the manner to be mentioned below:—

	Theory for pure KClO ₃ . Per cent.	Found. Per cent.
Chlorine	28.93	28.70, 28.82, 28.82, 28.79

As during the reduction free acid is formed in the chlorate solution, even if it is not added at the beginning, the use of potassium chromate as an indicator, together with direct titration with silver nitrate solution, failed to give satisfactory results. The figures obtained, however, were entirely satisfactory if the reduced solution was treated with an excess of silver nitrate solution of known strength, ferric alum added as an indicator, and the excess of silver nitrate determined by titration with ammonium sulphocyanate solution in the manner recommended by Volhard (*Annalen der Chemie*, cxc., 1).

The total chlorine being thus obtained, the amount present as chlorate per c.c. is easily found by subtracting from the total quantity the amount previously ascertained to be present in the form of chloride and hypochlorite.

It is also practicable to determine the hypochlorite by means of an arsenite solution, the chlorine present as chloride and hypochlorite together by means of silver solution as given above, and the hypochlorite and chlorate by allowing them to act upon potassium iodide in the way ordinarily described in the handbooks; and from the data thus obtained the amount of chlorine present in each form can then be calculated. I consider this process less convenient than the one already described.

The writer has used still another method which gives good results, but it is less rapid than those mentioned. After the determination of the hypochlorite and chloride present has been made, the total oxidising power of the original solution, due to the hypochlorite and chlorate contained in it, may be estimated by adding a known quantity to an excess of an acid ferrous solution, containing a known quantity of ferrous sulphate, boiling for a few moments in an atmosphere of carbonic acid, and titrating the unoxidised ferrous salt with potassium permanganate or potassium bichromate. The oxidising power of the original solution can be calculated from the

ferrous iron oxidised by it; and as the hypochlorite present is known, the chlorate present can be calculated.

Absorption of Chlorine.

In testing the efficiency of electrolytic chlorine generators it is most convenient to absorb the chlorine produced in sodium hydrate solution. The amount of chlorine already present in the alkaline solution should be determined by a preliminary analysis. The alkaline solution which absorbs the chlorine will contain it mainly as hypochlorite, but also as chloride and chlorate. A known fraction of the absorbing liquid is taken, made up to 1000 c.c., and of this 50 c.c. are measured and 20 c.c. of sulphurous acid solution and 5 c.c. of nitric acid added, the sulphurous acid removed by boiling, and the total chlorine is then easily found by the method described for the estimation of the total chlorine in the electrolysed solution, and from this the chlorine originally in the solution must be subtracted.

I see no reason why the methods given above may not be applicable to the analysis of bleaching powder in cases where the estimation of total chlorine and chlorate is desirable.—*Technology Quarterly*, iv., No. 4.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 30TH, 1892.

By WILLIAM CROOKES, F.R.S.,

and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, August 12th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the total 182 samples examined during the month, one sample had to be noted as "slightly," and six samples as "very slightly" turbid, consequent, doubtless, on the occurrence, occasionally, of violent rainfall. To the same cause also is doubtless attributable a somewhat lessened degree of freedom from colour-tint in the supply generally, the measurements of the colorimeter being appreciably affected by otherwise scarcely noticeable interferences with the transparency and brightness of the water.

Despite these circumstances, however, the general condition of the month's supply was entirely satisfactory, and in respect to the smallness of the proportion of organic matter present, as estimated by the combustion process, was even exceptionally so. The proportion of organic carbon present in different samples varied, however, within a wider range than usual. Thus, among the Thames-derived samples, the proportion ranged from a minimum of 0.040 part to a maximum of 0.152 part; while the proportion in the previous month's samples ranged only from

a minimum of 0.072 part to a maximum of 0.134 part in 100,000 parts of the water.

The mean proportion of organic carbon present in the Thames-derived supplies was found to be only 0.095 part, as against a mean for the month of June of 0.107 part, and for the previous three months, including June, of 0.117 part in 100,000 parts of the water. The mean proportion of organic carbon in the Thames-derived water furnished by the Chelsea Company was, moreover, quite exceptionally low, amounting only to 0.072 part, that of the New River Company's supply being 0.067 part in 100,000 parts of the water.

During the past month we have made an additional series of daily examinations of the unfiltered water of the Thames at Molesey. The proportion of organic carbon was found to range from 0.165 part to 0.195 part, with a mean of 0.182 part in 100,000 parts of the unfiltered water, as against the above mentioned mean of 0.095 in the filtered water distributed. The ratio of organic carbon to organic nitrogen in the unfiltered water was found to be substantially identical with that in the filtered water, being in the former case as 1:0.311 and in the latter case as 1:0.326.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.

THE SPECIFIC HEAT OF ATOMS, AND THEIR MECHANICAL CONSTITUTION.

By G. HINRICHS.

In my former paper I have shown that there is between the simple radicle (chemical element) and the complex radicle a mechanical contrast which obliges us to renounce the very general idea of considering the elements as radicles not yet decomposed.

The demonstration given of this principle is novel, but the fundamental principle has been laid before the Academy itself in the memorable discussion on the nature of the elements of chemistry in the Session of December 8th, 1873, by M. Berthelot, who said (*Comptes Rendus*, lxxvii., p. 1352, 1873):—

"In fact, the simple bodies, as we know them, possess certain positive characters which do not belong to the compound bodies, such as the relations existing between the specific heat of a body, its gaseous density, and its atomic weight; relations independent of its temperature."

This declaration of fact, concerning the rational bases of all scientific study of the unity of matter is defined in the following manner (*Loc. cit.*, p. 1356):—

"Between the compound bodies which we know and their polymers there exists this general relation, that the specific atomic heat of a polymer is approximately a multiple of that of the uncondensed body."

On the contrary, the atomic specific heat remains constant for the various elements whose atomic weights are multiples of each other. The same difficulties exist for the hypothesis of a simple body, the atomic weight of which would be the sum of the atomic weights of two others."

M. Berthelot returns to this general principle of thermo-chemistry in the following Session in these terms (*Loc. cit.*, p. 1401):—

"In sum, the study of specific heats, such as the most recent researches have brought to light, leads to the establishment of a positive character which distinguishes, as it seems to me, the simple bodies of chemistry from the compound bodies: it shows that no known compound body can be reputed of the same order as an actual simple body. The importance of such a character cannot be called in question; it increases in virtue of the mechanical

signification which the theories of the present day ascribe to the notion of specific heats. This is what I have endeavoured to bring forward."

The facts established are beyond all controversy; the general principle announced by M. Berthelot constitutes therefore, of necessity, one of the bases of the great problem of the constitution of matter. Every research into the mechanical constitution of the chemical elements ought to take this principle into consideration, and give its mechanical signification. To set aside this fundamental principle would be to avow non-comprehension of the problem, and to seek to discuss on astronomy whilst ignoring the movement of the earth. This is what has been done recently by some distinguished chemists.

There remains the question of the mechanical signification of this thermo-chemical principle of M. Berthelot. Let us give its elementary demonstration which results from my formulæ published in 1872 ("Beiträge zur Dynamik des Chemischen Moleküls," *Deutsch. Chem. Gesell.*, May 11, 1872), and 1873 (*Comptes Rendus*, lxxvi., p. 1358), and which agree with the general constitution of the atoms of the elements in my "Programme de la Mécanique des Atomes," of 1867:—

"Let m be the mass of an elementary atom (simple radicle), and v its maximum undulatory velocity. In like manner, for an atom composed of n atoms m , let M be the total mass and V the velocity of the centre of gravity. We shall have—

$$(117). \quad M = \Sigma m,$$

$$(118). \quad 2E' = \Sigma m v^2 + M V^2$$

if we call the total energy of the vibrations E' . For more complete formulæ I must refer to *Comptes Rendus* (lxvi., p. 1358, 1873) and to the recent edition of my "Beiträge" of 1872 (G. Fock, Leipzig, pp. 3—6, 1892).

But according to thermodynamics we have—

$$(119). \quad M V^2 = 2k T,$$

T being the absolute temperature, and k a constant. In like manner we have—

$$(120). \quad m v^2 = 2\rho k T,$$

where ρ is another constant.

We have then the expression of all the actual energy except that of rotation—

$$(121). \quad E' = k(1 + \rho n) T.$$

The atomic specific heat, representing the vibrations only, will therefore be—

$$(122). \quad s' = \frac{dE'}{dT} = k(1 + \rho n).$$

This formula shows that the specific heat of the atoms increases almost proportionally to the number, n , of the atoms contained in the compound or complex radicle.

For the chemical elements this atomic heat is, according to experiment, constant and independent of n . Therefore ρ ought to be null; that is to say, that the velocity of vibrations of the constituent atoms, m , ought to be null [see (120)].

The mechanical signification of Berthelot's thermo-chemical principle may, perhaps, therefore be formulated as follows:—

"In chemical compounds the atoms of the elements enter as integrant individualities, retaining a specific vibratory movement; but the atoms of the true chemical elements are solid or liquid bodies, the constituent atoms of which have no individual movements.

In presence of this general result, it is not surprising that the chemical elements have hitherto resisted all the efforts hitherto made for their decomposition. The establishment of the mechanical constitution of the elements has been the supreme object of my studies for thirty-eight years. I hope to be able to publish my final results before a year from the present date; but, in order to succeed, it will be necessary to establish several other laws of the mechanics of atoms. I must therefore resume

the study of the ebullition points as a function of the form of atoms of known composition. Having considered the terminal substitutions, I must study the central substitutions in an early study.—*Comptes Rendus*, cxv., p. 239.

ON A NEW CLASS OF COMPOUNDS, THE NITRO - METALS; AND ON THE PROPERTIES OF NITROGEN PEROXIDE.

By PAUL SABATIER and J. B. SENDERENS.

THE oxidising properties of nitrogen peroxide (hyponitric acid) are more active than those of nitric oxide, previously studied, and the products yielded are generally in a more advanced state of oxidation.

Lower Oxides.

Manganous oxide, MnO , in nitrogen peroxide is oxidised at about 350° , yielding manganese sesquioxide (manganese per cent—found, 69.6; calculated, 69.1).

Titanium sesquioxide is oxidised at 300° , as in air and nitric oxide, yielding white titanic acid, TiO_2 .

Tungstic bioxide (brown), TuO_2 , reacts below 300° with incandescence; the product is similar to that formed in air, i.e., yellow tungstic acid, TuO_3 , mixed with a little blue oxide.

Black vanadium oxide, Va_2O_3 , is oxidised at from 300° to 400° and is totally transformed into yellow-brown vanadic acid, Va_2O_5 .

Red cuprous oxide, Cu_2O , which is not affected by nitric oxide, is converted by nitrogen peroxide at 300° into black cupric oxide.

Metals.

Aluminium filings are not appreciably oxidised even at 500° .

Magnesium filings react only at dull redness, when they display a very energetic combustion.

Zinc is very regularly oxidised about 300° .

Lead is slowly oxidised above 200° , and yields white basic nitrate.

The metals obtained on reducing the oxides by hydrogen present a quite special interest.

Reduced nickel reacts with incandescence at 250° , yielding protoxide, which is merely greyish.

Reduced iron is oxidised with incandescence about 350° , yielding ferric oxide.

Reduced cobalt burns briskly at the common temperature in nitrogen peroxide, and forms black oxide, Cu_2O_5 .

Reduced copper is converted at 250° into black oxide, CuO , but in the cold it reacts upon nitrogen peroxide, giving a special compound which we shall describe in detail.

II.—Nitro-metals.

Pure dry nitrogen peroxide can fix itself in the cold upon certain metals, forming special compounds which we propose to call "nitro-metals."

Reduced copper absorbs in the cold the vapours of nitrogen peroxide with a disengagement of heat perceptible to the touch. When this action has ceased, there remains a maroon compound, the composition of which is represented by the formula Cu_2NO_2 . The increase of the weight of the copper during fixation yields an indirect method of analysis, which has been checked by the ulterior analysis of the product.

The compound reacts violently with water, yielding nitric oxide, which is entirely absorbable by ferrous sulphate, yielding a green liquid which contains copper nitrate mixed with a little nitrite. There remains a residue of copper almost absolutely pure. The proportion of copper dissolved varies, according to the duration of the reaction, from 11.1 to 13.4 per cent.

If heated in pure dry nitrogen, the substance disengages

nitrogen peroxide in abundance, and there remains copper mixed with a certain proportion of oxide; one-third of the oxygen is thus retained.

If it is heated in a sealed tube the same reaction takes place, and we may liquefy nitrogen peroxide in a refrigerated portion of the tube. A re-absorption takes place anew in part by the metal not oxidised.

The preparation of nitro-copper requires that the nitrogen peroxide must be free from traces of nitric acid which it may contain, and which is derived especially from the energetic action upon the caoutchouc connections. This nitric acid reacts upon the compound, which it gradually destroys with effervescence, forming the green nitrate. We may succeed in completely eliminating it by placing in front of the boats, in the reaction tube itself, a column of litharge followed by a column of phosphoric anhydride. The litharge absorbs the nitric acid, and the phosphoric anhydride takes up the water which may possibly have been formed by the reaction of the litharge.

Reduced cobalt, as it has been mentioned above, burns in the cold in the vapour of nitrogen peroxide. This ignition may be avoided by suitably diluting the vapours of peroxide with a current of pure dry nitrogen. We then observe a reaction absolutely similar to that given by copper; we find a disengagement of heat, which continues as long as the fixation takes place. When it has ceased nitro-cobalt remains as a black compound, the composition of which corresponds exactly to the formula CO_2NO_2 .

Its reaction with water is extremely lively, but less gas is given off than in case of nitro-copper. We obtain a rose coloured solution of cobalt nitrates containing very little nitrite. At the same time there occurs a precipitation of insoluble bluish green basic nitrite, which is found mixed with metallic cobalt.

Nitro-cobalt, if slightly heated in a current of nitrogen, evolves at first a little nitrous vapour, then almost immediately it deflagrates with an extraordinary lustre, leaving a residue of metallic chloride peculiarly oxidised. If it is mixed with a combustible matter, there occurs an explosive deflagration.

We are pursuing the chemical study of these compounds, and at the same time the preparation of new nitro-metals.—*Comptes Rendus*, cxv., p. 236.

THE SOLUBILITY OF THE PHOSPHORIC ACID OF BONE-MEAL.

By H. OTTO.

THE consumption of bone-meal in the West of Germany has declined so much during the last two years that producers find it difficult to dispose of a good product even at low prices. The cheapness of superphosphates, and especially the extraordinary demand for basic slag meal, are the principal causes.

Probably no manurial substance has given rise to so many publications and theoretical researches as basic slag. In P. Wagner's memoirs on this subject the phosphoric acid of basic slag is almost without exception represented as superior to the phosphoric acid of other manures. It is in the first place remarkable that in Wagner's comparative manurial experiments the efficacy of bone-meal takes so low a relative position. In these experiments it seems to have resulted that the phosphoric acid of bone-meal scarcely occasioned an increase of the crop, and that its efficacy was always less than that of the phosphoric acid of basic slag.

Quite opposite views are put forward in the publications of Prof. Marek, of Königsburg, and Prof. Holdeffeiuss, of Breslau. The latter, in his treatise on "Das Knochenmehl, seine Beurtheilung und Verwendung" (Bone-meal, its Valuation and Use), says (p. 168), referring to the experiments of Marek: "According to these decidedly

trustworthy results bone-meal has a considerable manurial value, so that it may be included among the most certain and efficient manures. This conclusion is the more trustworthy as it agrees with the practical experience of many decennia and is fully confirmed daily.

These contradictions can scarcely be accidental, and I can only assume that the bone-meal used in Wagner's experiments was not a good product. The chief part of the bone-meal at present met with in commerce is produced from bones which have been freed from fat by means of benzene. The meals are either simply ground bones, or mixtures of bone-meals freed from glue, and so called "stamp-meal," obtained in the manufacture of granulated bones. Of the mixtures of horn-meal, blood-meal, crude phosphates, and a little bone-meal, which unfortunately are also met with in trade, I am not about to speak. These occur now less and less frequently since several experimental stations have declared an energetic war against them.

The bone-meal obtained from bones deprived of fat contains always from 4½ to 5 per cent nitrogen, and 21 to 23 per cent phosphoric acid (P_2O_5), rarely more than 2 per cent of fat, generally less; all bone-meals containing less than 4 per cent N and 20 per cent P_2O_5 are not pure degelatinised meals, or the entire substance of the bone has not been used in their manufacture.

It is remarkable that such a bone-meal which, according to Heyden, Holdeffeiuss, Marek, &c., is an excellent manure, should prove inert according to Wagner.

When the basic slag in the state of meal was especially recommended to farmers as an especially effective phosphoric manure, it was sought to prove the solubility of the phosphoric acid by means of Wagner's citrate solution. In fact, the phosphoric acid of basic slag, if ground sufficiently fine, is to a great degree soluble in this citrate.

In the conviction that a bone-meal almost deprived of fat must give up its phosphoric acid to a slightly acid solution of ammonium citrate, I examined various samples of bone-meal exactly according to Wagner's citrate method as laid down on December 19, 1885, and found that according as the meal had been more or less finely ground from 8.05 to 9.15 per cent of the P_2O_5 was rendered soluble, or from 38.28 to 41.20 per cent of the total weight of the meal.

From these results it is clear that the phosphoric acid of bone-meal freed from fat, but not from gelatin, is very readily soluble. If we consider further that on account of the large percentage of gelatin the solubility in the soil will be increased by the products of decomposition formed during decay we may assume with certainty that such bone-meals must possess a considerable manurial value.—*Chemiker Zeitung*, August 6, 1892.

THE COMPOSITION OF ANCIENT MORTAR.

MR. JOHN HUGHES, F.C.S., has contributed to the *Builder* an article on this subject, from which we quote the subjoined analyses.

The author deduces the following practical conclusions from these analyses:—

1. That the actual amount of lime present in a mortar may vary very considerably, but that within certain limits the quality of the lime is of great importance as the quantity,—indeed, a smaller quantity of well-prepared good lime is much more effectual than a larger quantity of a badly prepared or naturally inferior lime.
2. That the proportions of sand may also vary considerably, even in really good mortar, and that while it is always desirable that it should be rough, irregular in size, and with sharp edges, rather than be smooth and round, still that, on the whole, the quality of the sand is not of so much importance as the quality of the lime.
3. That the presence of oxide of iron and alumina in a

Analyses of Ancient Mortar.

	No. 1. Tintern Abbey.	No. 2. Caerphilly Castle.	No. 3. Raglan Castle.	No. 4. Giant's Tank, Ceylon.	No. 5. Rochester Castle.	No. 6. Glastonbury Abbey.	No. 7. Glendalough Church, Ireland.	No. 8. Corfe Castle.
Probable date of erection, about A.D.	1269.	1200.	1200.	1250.	1088.	1246.	Not known.	1000.
Water (lost at 212° F.) . . .	1'72	2'60	1'36	1'18	0'36	4'96	0'55	2'42
Combined water	3'98	7'73	4'06	2'66	1'48	4'94	2'92	4'02
Lime**	18'84	13'49	30'68	16'24	28'67	36'46	10'59	31'05
Magnesia	0'32	1'87	0'25	0'36	0'18	0'45	0'43	0'28
Potash	0'02	0'22	0'15	0'30	0'16	0'33	0'25	0'20
Soda	0'27	0'29	0'45	0'17	0'24	1'18	0'13	0'15
Oxide of iron	1'99	3'61	1'35	2'20	0'40	3'60	1'58	0'95
Alumina	1'36	1'34	0'80	2'65	0'30	1'45	0'71	0'15
Sulphuric acid	1'37	0'34	0'86	0'58	0'29	0'89	0'32	0'26
Carbonic acid*	12'13	9'53	21'01	11'11	20'60	25'06	6'40	22'86
Chlorine	0'13	0'01	0'15	trace	0'10	0'88	0'14	0'65
Gelatinous silica, soluble in alkali	6'20	9'85	4'10	7'10	1'60	6'10	3'90	7'50
Insoluble matters (sand) . . .	51'67	49'12	34'78	55'45	45'62	13'70	72'08	29'51
	100'00	100'00	100'00	100'00	100'00	100'00	100'00	100'00
* Equal to carbonate of lime . .	27'56	21'66	47'75	25'25	46'81	56'95	14'54	51'95
Lime present as carbonate . .	15'43	12'13	26'74	14'14	26'21	31'89	8'14	29'09
Lime present as caustic . .	0'28	0'56	0'84	0'56	0'56	0'56	0'84	0'28
** Lime present as sulphate . .	0'95	0'23	0'60	0'40	0'20	0'62	0'22	0'18
Lime present as silicate and otherwise combined . .	2'18	0'57	2'50	1'14	1'70	3'39	1'39	1'50
	18'84	13'49	30'68	16'24	28'67	36'46	10'59	31'05

form readily combined with silica is not to be objected to in good building lime; indeed, that the purest limestones are by no means the best for making superior lime for building purposes.

4. That the higher the proportion of amorphous or gelatinous silica soluble in alkali the better the quality of the mortar, and as this kind of silica is associated originally with the lime, rather than with the sand, it becomes of the greatest importance that the character and composition of the lime intended to be used should be fully inquired into, and the best possible quality in the neighbourhood always selected by the architect and used by the builder.

CORRESPONDENCE.

WATER ANALYSIS.

To the Editor of the Chemical News.

SIR,—It is with extreme regret that I observe a commencement of the "water analysis" controversy in your columns.

To my mind it is not only useless but derogatory to English science to wage a bitter wordy war concerning the merits of two rival processes, neither of which does more than give an approximation to the quantities of certain substances, the presence of which is only circumstantial evidence of the character of a water.

Instead of wasting our time in acrimonious discussion, cannot we English chemists combine our forces and search for other processes giving more definite information? We have many reagents for separating nitrogenous organic substances, certain of which, I take for granted, furnish the strongest evidence of pollution. Among these reagents I may enumerate tannin, salts of mercury, bismuth, cadmium, &c., phosphotungstic acid, saturated solutions of ammonium sulphate, sodium chloride, &c., and others will readily occur to the minds of your readers.

Would not our position as scientific men be stronger and more dignified if we made attempts to gain informa-

tion on the above lines? As the work will be long and tedious we should combine, and even invite the co-operation of our foreign colleagues; thus we shall certainly spend our energies with more profit than by mere argument.—I am, &c.,

H. DROOP RICHMOND.

50, Clanricarde Gardens,
Bayswater,
August 29, 1892.

WATER ANALYSIS.

To the Editor of the Chemical News.

SIR,—In a letter which appears in your last number Mr. J. Alfred Wanklyn states that I have quite recently been made Chemical Adviser to the Local Government Board, that I am forcing my process of water analysis upon reluctant chemists, that the correction for experimental errors in my laboratory is "0.32 m.grm. of carbon and 0.045 m.grm. of nitrogen per litre of water," and that in certain experiments with sulphate of quinine "the experimental carbon and nitrogen agreed exactly with the calculated quantities, but the calculated quantities were wrongly calculated." I rarely notice Mr. Wanklyn's wild and erroneous utterances, but in this case must ask you to kindly allow me space to say that these statements are, one and all, absolutely false.—I am, &c.,

E. FRANKLAND.

Leamington, August 31, 1892.

SOLAR RADIATION.

To the Editor of the Chemical News.

SIR,—The question of what becomes of the superfluous heat radiated from the sun and apparently lost in space, meeting with no solid body to absorb it, is one that has long exercised the minds of thinking men. Such waste seems little in keeping with the law of the "conservation of energy which pervades all Nature."

Some years ago a solution of the difficulty was propounded by the late Sir W. Siemens, which, though ex-

trremely ingenious, did not strike one as very probable, though in the absence of any other, and coming as it did from so great an authority, was admitted by many as possible.

I do not know if it has ever been conjectured that the radiations are probably absorbed by the highly attenuated matter with which many suppose that the entire regions of space are filled. But may not such be the case, and is there any reason to the contrary? Gases and vapours are diathermanous in various degrees according to their nature, and according to the activity of the heat radiations which are transmitted through them; but they all surely must exert some absorbent effect, though the rise in temperature may be inappreciably small; if so, in infinite space all the heat would at length be taken up. If, then, the radiations are so absorbed, they go to increase the volume, though ever so imperceptibly, of the ultra-gaseous matter, and are utilised in increasing the trajectory of the vibrations of each of its material particles, so that the heat would not be wasted, but would be stored up in the universe perhaps to play its part in the production of fresh worlds or the evolution of new elements, and perhaps to be diffused again into space and to seek fresh matter with which to become associated. It is even conceivable that if the temperature of the sun and the other stars is maintained, as some persons suppose, by the impact of meteor swarms, the heat which has been absorbed by the ultra-gaseous matter contained in the limitless regions of space may by these means be restored to its original source in lapse of time.—I am, &c.,

F. MAXWELL LYTE.

London, Aug. 29, 1892.

ESTIMATION OF CAOUTCHOU.

To the Editor of the Chemical News.

SIR,—I am not aware of any method which enables us to estimate caoutchouc as a principle. It is usual in analyses to state the quantity by difference, but of course any substance present which disappears on combustion, &c., will make an article appear richer in caoutchouc than it actually is. Lead oxides are reduced by carbon and volatilised. Carbon and carbonic acid also disappear.

Presuming that the mat supplied by M. Guibal was vulcanised, how is 40 per cent caoutchouc estimated in presence of 15 per cent "vulcanised clippings"? In an uncured mixture it is possible by solvents to separate cured from uncured rubber if present.

Will two parts sulphur vulcanise forty parts caoutchouc in the presence of thirty-five parts litharge? It is well known that the sulphur used varies with the different descriptions of caoutchouc met with in commerce, and also with the same rubber according to its intended use. Litharge will take up more or less sulphur, leaving a diminished quantity for vulcanising. Sulphurous acid gas vulcanises, but it is doubtful whether the quantity formed would compensate for the sulphur lost as lead sulphide.

Again, why is lead estimated as litharge in a vulcanised mixture? or is lime present only as chalk? How can 2 per cent sulphur be fixed on when the mixture contains 15 per cent "vulcanised clippings." It is no less interesting to know how the 15 per cent was determined?

I may venture to say that 35 per cent litharge was a needless addition, and that it must have added to the expense of the mat in increasing its specific gravity, which is of fundamental importance, but which unfortunately is not stated.

The statements of M. Payen with respect to gutta-percha resins are unreliable. I have rarely met with a sample of raw gutta-percha containing less than from 45 to 55 per cent resins. A portion of this can be removed.

If a sample be boiled for some hours in a flask on a water-bath with an inverted condenser, and the operation

repeated with fresh spirit until it ceases to give up anything more, being carefully laminated before each boiling, it will require at least a week's boiling. The solvent may be either a mixture of alcohol and ether, which acts quicker, or a mixture of equal parts absolute alcohol and rectified spirit of wine.

In addition to the two resins named by Payen, alban (white resin) and flavan (yellow resin), a third resin is present, which is probably an oxidised gutta-percha. Neither of these resins are saponifiable in an aqueous solution of soda.

Alban and flavan may be partially separated from each other, as alban is soluble in boiling alcohol and deposits on cooling. Flavan remains in solution, and by concentrating a further deposit of alban takes place. Alban and flavan are soluble in alcoholic potash solution: the third resin is not soluble in this liquid, and so admits of separation.

The quantity of resins present in gutta-percha will vary with the methods of collecting; for instance, 80 to 90 per cent, consisting principally of alban, may be found in the gutta-percha recovered from the bark of these trees yielding good gutta-percha when the ladescent juice is drawn from the wood.

The resins are probably modifications of gutta-percha; by destructive distillation they yield products which are obtained when this substance is similarly treated.—I am, &c.,

ELECTRON.

Detection of Resorcine.—L. Reuter (*Pharm. Zeitung* and *Chemiker Zeitung*) dissolves 0.1 grm. of substance in 50 grms. potassa lye, heats a few c.c. of this colourless solution in a test-glass at the temperature of the water-bath, and adds a few drops of chloroform or bromoform, or a minute crystal of chloral hydrate or bromal hydrate. The liquid soon takes an intense red colour. This reaction, which is extremely sensitive, was indicated by Guareschi as far back as 1872.

Recognition of Furfural.—E. Nickel (*Chemiker Zeitung*).—The substance in question is submitted to dry distillation in a clean test-glass free from dust (Schiff) or cautiously heated with a small excess of concentrated sulphuric acid (Von Udransky). In either case there are formed vapours of furfural, which give a red colour to paper charged with salts of aniline or xylydine. If it is desired to detect furfural in solution, the reagents used are certain phenols (α -naphthol), phloroglucine, or biliary acids (cholic acid).

Meeting of the Association of Bavarian Chemists at Regensburg, August 2nd and 3rd, 1892.—Herr Stockmeier (Nuernberg) discussed the acidity of paper and the determination of mechanical wood-pulp. After describing the various methods proposed, he explained the injurious action which acidity in paper may occasion in many of its uses. S. Metzger treated on the decision upon vinegar. An essential condition in the preservation of vinegar is the use of clean, tightly closing casks. Still, in spite of all care, "vinegar-eels" (*Anguillula exophila*) make their appearance, and collect at the bottom of the casks, whence they are dislodged on agitation—as it is frequently practised on drawing samples—and become distributed through the entire cask. The assumption, however, that the origin of the eels is connected with impurities, or with an insufficient strength of the vinegar, is erroneous. Vinegar-eels may be found even in a 12 per cent "distilled vinegar." According to the researches of Pasteur we possess no other permissible process for preventing the development of vinegar-eels than Pasteurising. In the ensuing discussion Borgmann (Wiesbaden) pointed out that, according to Pasteur, the eels require air for their existence. If this condition is wanting they speedily perish. To a question put by Janke (Bremen) whether these eels occur in vinegar prepared from distilled vinegar, the author replied that this is not the case.—*Chemiker Zeitung*.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 4, July 25, 1892.

Certain New Observations on the Use of the Calorimetric Bomb.—M. Berthelot.—The author distinguishes three cases which require different conditions, i.e., fixed compounds, solid or liquid, combustible gases, and volatile combustible compounds.

Study of Boron Trisulphide.—Henri Moissan.—This paper will be inserted in full.

Researches on the Chemical Constitution of the Peptones.—P. Schutzenberger.—The author's first results refer to the fibrine of horses' blood and its transformation into peptone under the influence of the pepsine of commerce in presence of hydrochloric acid. Peptonised fibrine, taken in its totality, differs from the initial fibrine only by the elements of water. It is not a homogeneous product, but may be split up by various methods into distinct products, the examination of which will form the subject of a future memoir.

Formation-Heat of Permolybdic Acid and the Permolybdates.—E. Péchard.—Permolybdic acid is formed with the absorption of heat. Its formation necessitates the intervention of extraneous energy, and in its production this energy is supplied by the heat liberated in the decomposition of oxygenated water.

Crystalline Mercury Phosphide.—M. Granger.—At ordinary temperatures, whether under normal pressure or in sealed tubes, phosphorus has no action upon mercury. The author has obtained the compound Hg_3P_2 by causing phosphorus iodide and mercury to react in sealed tubes at from 275° to 300°. The compound is permanent in the cold, but in heat it is decomposed into its elements. It ignites if heated in contact with air, and if mixed with potassium chlorate it detonates under the hammer. Nitric and hydrochloric acid have no action upon it, but it dissolves easily in *aqua regia*.

Mineralising Action of Ammonium Sulphate.—T. Klobb.—On treating copper salts with ammonium sulphate, the author has obtained in succession according to the temperature a double copper ammonium sulphate; (2) the sulphate SO_4Cu ; (3) basic sulphate $2CuO, SO_3$, and lastly cupric oxide. The double sulphate forms transparent light green prisms, about 1 m.m. in length, and of specific gravity 2.85. The author is further studying the action of ammonium sulphate upon the salts of chromium and uranium.

Micrographic Analysis of Alloys.—Georges Guillemin.—The researches of MM. Osmond and Werth undertaken to determine the structure of cast steel have led the author to make similar investigations of the industrial alloys of metals other than iron. He attacks a polished surface of such alloys either with cold dilute nitric acid or with sulphuric acid (1:10) under the influence of a weak electric current, and examines the surfaces with the microscope. The images obtained, which are afterwards photographed, are always invariably the same for any given alloy. The microscopic examination of surfaces of brass or bronze show accurately if aluminium or phosphorus has been added. If a brass contains aluminium the grooves or furrows observed take constantly the form of veins of marble or conglomerates. This holds good even if the aluminium is in such minute quantities that its presence is not readily detected by the methods of analytical chemistry. In fine, micrographic analysis renders it possible to determine rapidly and summarily the nature of a bronze or other alloy by the simple inspection of a surface polished and corroded, and

to recognise if the alloy has been simply cast or if it has been only stamped, laminated, or drawn.

Homopyrocatechine, and on its Two Nitro-derivatives.—H. Cousin.—The composition of the two compounds is respectively represented by the formula $C_7H_7NO_4$. The second compound is an isomer of the former. It melts at about 180°, whilst the former melts at 79° to 80°.

New Class of Compounds, the Nitro-Metals, and on the Properties of Nitrogen Peroxide.—Paul Sabatier and J. B. Senderens.—(See p. .).

The Specific Heat of Atoms and their Mechanical Constitution.—G. Hinrichs.—(See p. .).

Monopropylurea and Non-Symmetric Dipropylurea.—F. Chancel.—The former compound is neutral to litmus; it melts at 107° when quite dry, and it is very soluble in water and alcohol. The nitrate and oxalate are very soluble in water, out of which they crystallise badly. They are also very soluble in alcohol, on the evaporation of which the nitrate yields fine needles. The non-symmetric dipropylurea is also neutral to litmus; it melts at 57° and is very soluble in water and alcohol, sparingly soluble in saturated solutions of potassium sulphate. The neutral oxalate is sparingly soluble in water, from which it crystallises in fine needles; it has an acid reaction with litmus. The nitrate is a non-crystallisable syrup.

The Composition of Fossil Bones and the Variation of their Proportion of Fluorine in the different Geological Epochs.—Ad. Carnot.—The author finds in the specimens which he has examined a progressive increase of fluorine with the age of the specimen. The proportion of fluorine is in many fossil bones 10 or 15 times as great as in modern bones, referred to the same weight of ash. He suggests that a determination of fluorine may assist in fixing the age of bones.

Distribution and State of Iron in Barley.—P. Petit.—Almost all the iron is found in barley in the state of nucleine.

The Comparative Toxicity of the Alkaline and Earthy Alkaline Metals.—Paul Binet.—The author's experiments with lithium, sodium, potassium, magnesium, calcium, strontium, and barium, in the state of chlorides, have been made by the subcutaneous method upon warm blooded animals and upon frogs. The general results are:—(1) The most general effect exerted by metallic salts upon the organism is the loss of excitability of the nervous system, central and peripheric, and then an alteration of muscular contractility. (2) This ultimate stage is preceded by disturbances of respiration and of the heart, which may occasion a rapid death before any other symptom. In warm-blooded animals we may, even on subcutaneous injection, observe gastro-intestinal troubles: vomiting, diarrhoea, especially with barium and lithium. (3) In addition to their general action the metals are distinguished from each other by their particular characters, which render it possible to establish a relation between the nature of the physiological action exerted by the metal and the place which it occupies in the chemical classification. (4) The natural group, lithium, sodium, potassium, is characterised by the stoppage of the heart in diastole, weak motor inertia without contractions; the group calcium, strontium, barium, is characterised by the stoppage of the heart in systole, and the tendency to contractions especially in the case of barium. (5) Calcium is further distinguished by the special action which it exerts upon the nerve centres, a state of torpor with retention of reflex excitability and sensitiveness. (6) Magnesium approximates to the first group by the stoppage of the heart in diastole, but it deviates from the other metals by the early paralysis of the peripheric nervous system. It is a motor-paralyser like curare, but it is distinguished from the latter by interfering less readily with respiration. (7) According

to the intensity of their poisonous action, studied upon the frog, these metals may be classified in the following decreasing order: lithium, potassium, barium, very poisonous; calcium and magnesium, much less poisonous; strontium, slightly poisonous; sodium, scarcely poisonous at all. Among the mammalia the order is rather different; for them barium is by far the most poisonous. (8) Contrary to the law proposed by Rabuteau, there is no constant relation between the toxicity of a metal and its atomic weight; this relation cannot even be found among the elements of the same group. (9) The author refers to the special tolerance of the organism for sodium as being probably due to ancient adaption to a saline medium.

Colourless Globuline possessing a Respiratory Function.—Dr. A. B. Griffiths.—This globuline has been extracted from the blood of *Patella vulgata*. Its molecule contains no metal, and it possesses the same properties of oxygenation and deoxygenation as do hæmoglobine and hæmocyanine. The author names this compound achroglobine, and assigns to it the formula $C_{523}H_{761}N_{196}SO_{140}$.

Vol. cxv., No. 5, August 1, 1892.

On Boron Pentasulphide.—Henri Moissan.—Boron pentasulphide possesses properties which distinguish it clearly from the trisulphide. Its melting-point is 390° , whilst the trisulphide begins to melt at 310° . Its manner of fusion differs also from that of the trisulphide; it does not pass through a pasty condition, but becomes immediately liquid as soon as the temperature of 390° is reached. In contact with water it is resolved at once into boric acid, sulphuretted hydrogen which escapes, and sulphur which is deposited, whilst the pure trisulphide never gives a deposit of sulphur. Whilst the trisulphide is not attacked by mercury and silver, even at a dull red heat, this new compound is easily attacked by these metals, forming boron trisulphide and a metallic sulphide. The action of mercury is very characteristic. The vapour of mercury attacks this compound with incandescence; mercury sulphide distils, and there remains melted boron trisulphide.

Constitution of Pyrogallol.—M. de Forcrand.—A thermo-chemical paper, which does not admit of useful abstraction.

On Cascarine.—M. Leprince.—Cascarine is a proximate principle obtained from the bark of *Rhamnus prushiana*, known by the Spaniards as *Cascara sagrada*. It forms prismatic needles of an orange yellow. It is tasteless and inodorous, soluble in alkaline solutions, with a dark purple-red colour. It is insoluble in water, soluble in pure alcohol and in ether-alcohol, less soluble in chloroform. If perfectly dried its composition is $C_{12}H_{10}O_5$. The author raises the question whether cascarine is identical with rhamnatine, or if they are merely isomeric.

Properties of the Vapours of Formal or Formic Aldehyd.—F. Berlioz and A. Trillat.—These vapours diffuse themselves rapidly in the animal tissues, which they render incapable of putrefaction. Even in slight proportions they oppose the development of bacteria and other organisms. They sterilise in a few minutes substances impregnated with the bacillus of Eberth and that of splenic fever. The vapours are not poisonous unless inhaled for some minutes and in large quantities.

MISCELLANEOUS.

The Wiesbaden Laboratory.—According to the *Chemiker Zeitung* the laboratory of Prof. Dr. R. Fresenius has, during the summer term, been attended by fifty-eight students. Of these forty-three are from Germany; two

each from Belgium, Sweden, and North America; one each from Austria, Switzerland, Holland, France, Spain, England, Russia, Roumania, and Java. There are three assistants in the tutorial laboratory, three in the experimental station, and sixteen in the various departments of the laboratory of research. The staff includes, in addition to the Principal, Professors H. Fresenius and Borgmann, Drs. W. Fresenius, E. Hintz, Frank, and the architect Brahm. The next term begins on October 17th. In addition to scientific work (pure) there have been conducted, during the summer, numerous investigations in the interest of commerce, the arts, mining, agriculture, public health, and justice.

Commercial Potassium Cyanide.—According to the *Chemiker Zeitung* (1892, No. 64), Dr. Kayser, of Nurnberg, read a paper on this subject before the eleventh meeting of the "Free Association of Bavarian Representatives of Applied Chemistry." The kinds of potassium cyanide at present generally met with in commerce consist largely of a mixture of potassium cyanide and sodium cyanide. This circumstance must be remembered in examinations of potassium cyanide. If we simply determine the quantity of cyanogen, and calculate the result as potassium cyanide, a commercial sample containing 15 per cent impurities may easily be reported as potassium cyanide of 100 per cent. The presence of considerable quantities of sodium cyanide is further not indifferent in many technical applications. Thus, in preparing galvanic gold-baths from gold as anode in a solution of potassium cyanide and sodium cyanide by means of the galvanic current, there is obtained not the readily soluble potassium aurocyanide, but the very sparingly soluble sodium aurocyanide. The latter on its origin is at once deposited on the anode, and we do not succeed in obtaining a useful gold-bath. According to the view of the speaker it is possible that the advice of Wagner has been followed in the manufacture of the ferrocyanide. Wagner, namely, from technical reasons, recommended the use of a mixture of potash and soda, and that the resulting mixture of potassium and sodium cyanides should be sold under the name of "cyanogen salt." Prof. Fresenius confirmed the presence of sodium ferrocyanide in the potassium ferrocyanide of commerce.

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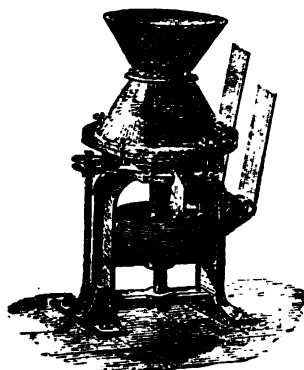
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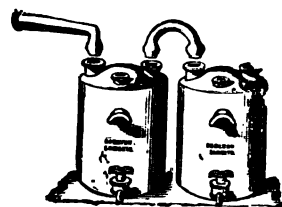
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THE CHEMICAL NEWS.

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(STUDENTS' NUMBER).

ADDRESS TO STUDENTS.

It has often been asked why so few of the best minds in this country turn their attention to scientific research? The answer commonly and bluntly given is because research does not pay. The emoluments which fall to the lot of the greatest discoverer are trifling compared with those which he might have realised with less labour in various other departments of activity. Had he given his mind to theology he might have become a prelate. Law might have showered upon him not merely heavy fees and refreshers, but might have earned him a title. But Science had nothing to offer but the gratification of the love of truth. Sir Isaac Newton, we are told, had he been living in these days could scarcely have earned salt to his food. Darwin, so far from being enriched by his discoveries, could not have carried out his investigations except he had been born to an ample fortune. He received no pay for serving on the memorable voyage of the *Beagle*, but had, in vulgar phrase, to find himself. Nor was the discoverer compensated by honours or social position for the lack of material rewards. We have, indeed, had amongst the aristocracy men of genius, such as Robert Boyle and Henry Cavendish. The names of Lords Rayleigh and Walsingham are honourably known. But these *savants* inherited their peerages, and would have held the very same rank had they been the most utter blockheads. In short, until within the last few years the highest rank which a *savant*, as such, could hope to reach was that of baronet.

As a matter of course, young men were warned by their friends not to enter upon so barren a career. We are, indeed, told that men of Science should be above all such considerations. Unfortunately men of Science have the same wants, the same aspirations as other mortals, and when they find that those wishes cannot be gratified in the service of Science they are very apt to look elsewhere.

But now a new day seems to be dawning. We do not know—and we care little—to whose initiative the change is owing, whether to Her Majesty personally, to the late administration, or to their successors. All we hope is that the change may be permanent, and that an honourable ambition may find its reward in the realms of Science as readily as in those of law or finance.

No one, we trust, will be perverse enough to hint that we advise young men to study physics or chemistry in view to a possible peerage. Such a reward will scarcely fall to the lot of one in ten thousand. But the honours conferred upon Lord Kelvin and Lord St. Andrews,—honours which can be understood even by the most stolid Philistine,—will irradiate and encourage even the humblest of their colleagues.

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must have passed the Matriculation Examination. No exemption from this rule is allowed on account of Degrees obtained or Examinations passed at any other University. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June.

The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must, not less than five weeks before the commencement of the Examination, apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the commencement of the Examination, accompanied by a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination. As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Registrar, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination for the first time must pay a Fee of Two pounds to the Registrar. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him, but he shall be allowed to enter for any subsequent Matriculation Examination upon payment, at every such entry, of an additional Fee of one pound, provided that he comply with the Regulations in the preceding paragraph.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin. Any one of the following Languages:—Greek, French, German, Sanskrit, or Arabic. The English Language, and English History, with the Geography relating thereto. Mathematics. Mechanics. One of the following branches of Science:—Chemistry, Heat and Light, Magnetism and Electricity, Botany.

The Examination in Chemistry is—Chemistry of the Non-metallic Elements; including their compounds, their chief physical and chemical characters, their preparation, and their characteristic tests.

A Pass Certificate, signed by the Registrar, will be delivered to each candidate after the Report of the Examiners has been approved by the Senate.

If in the opinion of the Examiners any candidates in the Honours Division of not more than twenty years of age at the commencement of the Examination possess sufficient merit, the first six among such candidates will receive an Exhibition of thirty pounds per annum for the next two years; the second among such candidates will receive an Exhibition of twenty pounds per annum for the next two years; and the third will receive an Exhibition of fifteen pounds per annum for the next two years; such exhibitions are payable in quarterly instalments provided that on receiving each instalment the Exhibitioner declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific M.B. Examination, and Intermediate Examination in Medicine, within

three academical years from the time of his passing the Matriculation Examination.

Under the same circumstances, the fourth among such Candidates will receive a prize to the value of ten pounds in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of five pounds in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will be held July 16, 1893.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. EXAMINATION.

The B.Sc. Examination will be held October 15, 1893.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

Examination for Honours.

The examination for Honours in Chemistry will take place on Monday and Tuesday in the week following the Examination for Honours in Mathematics; on Monday by printed papers (chiefly on Organic Chemistry), and on Tuesday by practical examination in Qualitative and Quantitative Analysis.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with this statement he shall transmit an original printed Dissertation or Thesis (at least six copies) treating scientifically some special department of the subject so named, embodying the result of independent research, or showing evidence of his own work, whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within

the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, and with especial reference to his Dissertation or Thesis.

Candidates for the Degree of D.Sc. will be expected to be so fully conversant with the branch of Science they profess as to be able, if required, to satisfy any test of their acquirements in that branch that it may be thought expedient to apply.

In October, 1892, modifications of the Regulations for the Degree of D.Sc. will come into operation, particulars of which can be obtained of the Registrar.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.*

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the third Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination. Not less than five weeks before the commencement of the Examination he must apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the Examination, accompanied with the candidate's fee.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry.—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years, passing at least two examinations in Arts, and one in either Mathematics, Natural Science, Law, Modern History, or Theology, when, if he obtain a first, second, or third class, he can take his B.A. Degree; if he do not gain such honour he has to pass a third examination in *Literis Humanioribus*.

The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Scholarships of about the value of £75 are obtainable at Christ Church, Magdalen, and other colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the University Calendar; from the professors; and from the Sub-Librarian in the Radcliffe Library or the Museum.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry.—G. D. Liveing, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy.—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in the first or third term of residence, or, through the Oxford and Cambridge Schools Examination Board, or through the Senior Local Examinations, before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £10 a year, are chiefly given for mathematical and classical proficiency. Scholarships are given for Natural Science in Trinity, St. John's, St. Peter's, Clare, Christ's, Sidney, Pembroke, Caius, and Downing Colleges; the examinations being in December, at Easter, and in June and October.

* Candidates who pass in all the subjects of the Preliminary Scientific (M.B.) Examination, and also pass at the same time in the Pure and Mixed Mathematics of the Intermediate Examination in Science, or who have previously passed the Intermediate Examination in Arts, are admissible to the B.Sc. Examination.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN. TRINITY COLLEGE.

Professor of Chemistry.—J. Emerson Reynolds, D.Sc., M.D., F.R.S., V.P.C.S.

Assistant Lecturer.—Emil A. Werner, F.C.S., F.I.C.

Demonstrator.—William Early, F.I.C.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 1st of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy.*—Elementary, first year; advanced, second year.
2. *Organic Chemistry.*—General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The *Summer Course of Practical Chemistry for Medical Students* begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

KING'S COLLEGE.

(DEPARTMENT OF ENGINEERING AND APPLIED CHEMISTRY).

Professor of Chemistry.—J. M. Thomson, F.C.S.

Demonstrator of Practical Chemistry.—G. S. Johnson, F.C.S.

Assistant Demonstrator.—Herbert Jackson, F.C.S.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a View of the Forces which concur to the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic elements and their principal Compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *visd voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis. Any Student of this Department may be admitted to this Class at any period of his study on payment of an extra fee.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s. od.; per ann., £8 8s. od.; Practical Chemistry per term, £4 4s. od.; per ann., £10 10s. od.; Experimental and Analytical Chemistry—Daily attendance: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three months, £6 6s.; Six months, £11 11s.; Nine months, £15 15s.

Rules as to Admission of Students.

I. The Academical Year consists of Three terms: Michaelmas Term, from beginning of October to the week before Christmas; Lent Term, from the middle of January to the week before Easter; Easter Term, from Easter to the beginning of July.

II. The days fixed for the Admission of New Students in the Academical Year 1892-93, are Tuesday, October 4, Wednesday, January 11, and Wednesday, April 19.

METALLURGY.

Professor.—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

PHOTOGRAPHY.

Lecturer.—Prof. J. M. Thomson, F.R.S.E., F.C.S.

Arrangements are made for a complete Course of Instruction in Photography to the students of the third year. A glass house has been erected, and in connection with it a Laboratory for the preparation of Photographic Chemicals. Students entering to this department will be afforded every facility for practising the Art in all its branches.

In addition to the regular College Course in Photography occasional classes are formed, consisting each of about six gentlemen, who meet twice a week. The fee for private instruction is £5 5s. for ten lessons, or £10 10s. for three courses. There is in every case a charge of £1 each course for chemicals.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the months from October to March, inclusive, and during the months of April, May, and June.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professor.—William Ramsay, Ph.D., F.R.S.

Assistant Professors.—R. T. Plimpton, Ph.D., and J. N. Collie, Ph.D.

Assistants.—H. W. Piñon, B.Sc., and P. B. Williams.

The Session is divided into three Terms, as follows, all the dates being inclusive :—

First Term, from Monday, October 3rd, until Wednesday, December 21st;

Second Term, from Tuesday, January 10th, 1893, till Saturday, March 25th;

Third Term, for Lectures, from Tuesday, April 18th, till Friday, June 30th. Class Examinations begin on Monday, June 19th.

Junior Courses.

First Term : Tuesday, Thursday, and Saturday, at 10, commencing October 7, 1892. Third Term : Tuesday and Thursday at 10, Friday at 4, beginning April 14th, 1893. Fee :—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

Senior Course of Chemistry.

First and Second Terms : Inorganic.—The Class meets four times a week : Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises, commencing October 6th.

Fee :—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Int. Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9. The hour will be altered by special arrangement with the class if necessary.

Fee :—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

Organic Chemistry.

Tuesday and Thursday, at 9, in the First Term; Tuesday, Thursday, and Saturday, at 10, in the Second Term; and Tuesday and Thursday, at 9, and Saturday, at 11, in the Third Term. The hour of meeting will be altered should the class desire it.

This Course of Organic Chemistry is intended for those who in studying the subject have not a Medical Examination chiefly in view. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course during the Second and Third Terms, instead of the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee :—For the Course, £6 6s.; for the Second and Third Terms, £4 14s. 6d.; for a Term, £2 12s. 6d.

Practical Class.

First and Second Terms, Tuesday and Thursday, at 11, commencing October 7th.

Fee, including cost of materials, £5 5s.; for a Second Course, £3 3s.

The Course includes the Practical Chemistry required at the Preliminary Scientific and Intermediate Science Examinations.

Senior Practical Class.

Wednesdays from 2 to 4 and Saturdays from 10 to 12 during the Third Term.

Fee :—(Including cost of materials) £5 5s.; for a Second Course, £3 3s.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees : for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week :—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London :—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

Students who wish to attend the Lectures on Chemical Technology may acquire here the requisite knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

A Gold Medal and Certificates of Honour are competed for by first year's Students. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1892-93; also the Clothworker's Scholarship of £30.

Chemical Technology.

Lecturer, Watson Smith, F.I.C., F.C.S.

Courses of Lectures will be given on the following subjects :—Manufacture of Sulphuric Acid, Alkali, &c. Fuel and Gas Manufacture. Chemical Technology of Building Materials. Methods for the Technical Chemical Analysis of Raw and Manufactured Products. Coal tar Products and Colours. Applications of Chemistry to Engineering. Methods of Technical Chemical Analysis.

Evening Lectures will be given by gentlemen qualified by practical and theoretical acquaintance with special subjects, and occasional visits to Works will be arranged.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor.—T. E. Thorpe, Ph.D., B.Sc., F.R.S.

Assistant Professor.—W. P. Wynne, B.Sc., A.R.C.S.

Demonstrators.—H. Chapman Jones and A. E. Tutton.

Assistants.—G. S. Newth, J. W. Rodger, and W. Tate.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. But students who are not candidates for the Associateship are permitted to take up the course of instruction in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Royal College of Science is given in one or more of the following divisions :—Mechanics, Physics, Chemistry, Biology, Geology, and Agriculture, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins on the 5th of October and ends about the middle

of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first two years and in those of the special division he selects for his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the final examination in it receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
Chemistry	3	13
Physics	5	12
Biology with Botany ..	5	12
Geology with Mineralogy ..	4	8
Mechanics	4	6
Metallurgy	4	13
Mining	4	
Agriculture	4	
Astronomical Physics	2	3

Agricultural Chemistry, per term, £13. Mathematics and Mechanical Drawing, £3 per term. Geometrical Drawing £3 per session. Freehand Drawing, £1 per term.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the courses. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half the foregoing charges.

Associates of the Royal College of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

Bona fide teachers qualified to earn payments for teaching Science according to the rule of the Science Directory may attend any course of lectures on the payment of £1.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 200 teachers are admitted to them, and they receive 3rd class railway fare to and from South Kensington, and a bonus towards their incidental expenses of £3 each. (See Science Directory.)

Working Men's Lectures.—Notification of these will be given in the newspapers.

THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Fifty-first Session will commence on Wednesday, October 5th, 1892. Entries not previously arranged with the Dean or Secretary may be made between 10 a.m. and 5 p.m. on that day.

Officers of the School:—Prof. Dunstan, M.A., F.I.C., Chemistry (Dean); Prof. Atfield, Ph.D., F.R.S., F.I.C., Practical Chemistry; Prof. Green, M.A., B.Sc., F.L.S., Botany; Mr. Joseph Ince, F.L.S., Pharmacy and Practical Pharmacy; Mr. Henry George Greenish, F.I.C., F.L.S., Materia Medica.

Entries may be made for single classes. A bench in the chemical laboratories can be engaged at any time for any number of hours daily or days weekly for any period. Students are recommended to join the Lecture classes on Chemistry and Physics in October, but other convenient periods are the beginning of January or the commencement of the Second Course in April. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies. Certificates of attendance on the Courses of Pharmacy also are accepted by the conjoint Board.

For Prospectuses, &c., apply to Mr. F. W. Short Secretary to the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

Professor.—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Göttingen), F.I.C.

Demonstrator.—A. W. Warrington, M.Sc. (Vic.), F.I.C.

The College is open to male and female students above the age of sixteen years. The Session commences on Thursday, September 29, on which day all Students will be expected to meet the Professors in the Library of the College.

Lecture Courses.—(1) Matriculation Course; two lectures weekly during the Lent and three during the Easter Term. (2) Intermediate Science Pass Course; three lectures weekly during the Lent and Easter Terms. For those Students who have selected Physics or Botany instead of Chemistry at the Matriculation Examination, an Introductory Course of three lectures weekly will be delivered during the Michaelmas Term. (3) Intermediate Science Honours Course; two lectures weekly during the Lent and Easter Terms. (4 and 5) B.Sc. Pass and Honours Courses; each three lectures weekly throughout the Session.

Laboratory Courses.—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged to suit the requirements of the individual Student.

Students intending to proceed to the M.B. or B.Sc. Degree of the University of Edinburgh may count one or two years' residence respectively spent at this College.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 10s. per term, and for twelve hours, 20s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 20, and

exhibitions are awarded at the end of the Session on the results of the class examinations.

The Chemical Laboratories in connection with this College have been recently built, and are fitted with every convenience for the prosecution of chemical studies.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, George McGowan, Ph.D., F.R.S.E. Assistant Lecturer in Agricultural Chemistry, C. F. Archibald.

Physics.—Professor, Andrew Gray, M.A., F.R.S.E. Assistant Lecturer and Demonstrator, R. W. Stewart, B.Sc.

The Session opens October 4th, 1892. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the London University Matriculation Examination. Fee for the Term £2 2s. A class for revision of Matriculation Work will be held during the Summer Term. Fee for the Term, £1 1s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Term £2 2s.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s.

Medical Course.—Inorganic and Organic Chemistry. Fee for the whole Course, £4 4s.

Agricultural Chemistry.—Fee, £1 1s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, and Zoology Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for two years of the three years' degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE.

Professor.—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrator.—E. P. Perman, D.Sc., F.C.S.

The Session commences October 3rd, and terminates on June 23rd, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 55 lectures, and will cover the subjects prescribed for the London University Matriculation examination. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of 90 lectures in continuation of the Junior Course, and, together with laboratory practice, will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee £3 3s.

The Senior Course includes some 90 lectures devoted to Organic Chemistry; Fee, £3 3s.

An Elementary Organic Course of 10 lectures, and a course of 30 lectures on Qualitative and Quantitative Analysis will also be given.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 4.30; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Professors Thompson and Parker are recognised by the Universities of Edinburgh, Glasgow, and Aberdeen as teachers in Chemistry and Natural History respectively, so

that registered Medical Students can spend one year of their course at the University College, Cardiff. The College is also recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of London or the Medical Courses at the Universities of Edinburgh, Glasgow, and Aberdeen, may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Female Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry.—Sydney Young, D.Sc.

Lecturer.—Arthur Richardson, Ph.D.

The session 1892-93 will begin on October 5th. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratory. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Bristol Medical School, which is incorporated with the College. Several Scholarships are tenable at the College. Full information may be obtained from the Secretary.

DAY LECTURES.

Inorganic Chemistry.

The Courses treat of the Principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Junior Course.—Two Lectures a week will be given during the First and Second Terms.

Senior Course.—Three Lectures a week will be given throughout the Session.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Lectures will be given during the Second Term on Tuesdays and Thursdays at 10 o'clock; during the Third Term on Mondays, Wednesdays, and Fridays at 10 o'clock. Fee, £3 3s.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research.

Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. The Laboratory is under the immediate supervision of the Professor and the Lecturer. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session ..	15	13	10	7½	5
„ Two Terms ..	11	9	7½	5½	4
„ One Term ..	6	5	4	3	2
„ Month ..	3	2½	2	1½	—

Students may arrange to divide their days of laboratory work into half-days.

Photographic Chemistry.

Special arrangements can be made with regard to instruction in this subject.

Chemical Scholarship.—Among others, a Chemical Scholarship of £25 is offered for competition.

EVENING LECTURES.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

MASON SCIENCE COLLEGE, BIRMINGHAM.

Professor.—W. A. Tilden, D.Sc. Lond., F.R.S., F.I.C. **Assistant Lecturers.**—W. W. J. Nicol, M.A., D.Sc. Edin., F.I.C., and Thomas Turner, Assoc.R.S.M., F.I.C. **Demonstrator.**—Harold G. Colman, Ph.D., M.Sc. Vic. The Session will be opened on Friday, September 30th, 1892.

Elementary Course.

Forty Lectures adapted to the requirements of beginners will be given in the Winter and Spring Terms. A Second Course of Twenty Lectures, having reference only to the subjects included in the syllabus of the Matriculation Examination of the University of London, will be given in the Summer Term. Lecture days—Wednesdays and Fridays at 11.30, Thursdays at 3.30.

Persons entirely unacquainted with Chemistry are recommended to attend the first of these Courses before entering for the General Course, which commences in October. Candidates for the Matriculation Examination of the University of London are advised to attend both these Courses.

General Course.

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on Inorganic Chemistry (Winter and Spring Terms).

Candidates for Intermediate Examinations in Medicine will in general require only that part of the course (Summer Term) which relates to Organic Chemistry.

The full course, extending over three terms, will also satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About eighty lectures on Inorganic Chemistry and Chemical Philosophy will be given on Mondays, Tuesdays, Wednesdays, and Thursdays from October to December,

and on Mondays, Tuesdays, and Wednesdays from January to March, at 9.30 a.m. A Tutorial Class is held in connection with this Course once a week throughout the Session. Fee, £5 5s. for the course.

2. April to June (Summer Term). About thirty lectures will be given on Elementary Organic Chemistry, or the chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Tuesday, Wednesday, and Thursday at 9.30 a.m. Fee, £1 11s. 6d.

Advanced Course.

An Advanced Course for the study of Theoretical Chemistry and those parts of the subject which are required for the degree of B.Sc. in the University of London will meet once or twice a week. Fee for the session, £3 3s.

Laboratory Practice.

The College Laboratory is open daily from 9.30 to 5, except on Saturdays, when it is closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the Mason College Laboratory. Fees:—

	All day.	Three hours per day.
One Term ..	7 guineas	4½ guineas
Two Terms ..	13 „	8½ „
Three Terms ..	18 „	12 „

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Metallurgy.

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each course. A more advanced course upon selected subjects is also given by Mr. Turner, the Lecturer in Metallurgy.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c.

Evening Classes.

Several Courses of Evening Lectures are arranged during the Winter and Spring Terms of each session. The subjects are treated in a less technical manner and the fees are nominal.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor.

BRADFORD TECHNICAL COLLEGE.

CHEMISTRY AND DYEING DEPARTMENT.

Professor.—Christopher Rawson, F.I.C., F.C.S. (temporarily, until the appointment of successor).

Demonstrator.—E. E. Milnes, F.C.S.

Lecturer on Botany and Materia Medica.—William West, F.L.S.

The school year is divided into three terms. The Session commences on September 12th and terminates on July 7th. The course of instruction extends over two years, and embraces Lecture Courses on Inorganic and Organic Chemistry, the technology of the textile fibres, mordants, natural and artificial colouring matters,

technical analysis, and laboratory practice in analytical chemistry, chemical preparations, and dyeing. Inclusive fee, £4 4s. per term.

During the first and second terms Evening Classes are held for the benefit of persons engaged during the day and for pharmaceutical students.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor.—Prof. E. Kinch, F.C.S., F.I.C.

Assistants.—James Hendrick, B.Sc. Lond., A.I.C., and W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation and stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY.

THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry.—Arthur Smithells, B.Sc. Lond., F.I.C.

Lecturer in Organic Chemistry.—Julius B. Cohen, Ph.D., F.I.C.

Assistant Lecturer in Agricultural Chemistry.—Herbert Ingle, F.I.C.

Demonstrator.—C. F. Baker, Ph.D., B.Sc.

The Session begins October 10, 1892.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m., from October to the end of the second term, and during part of the third term. Fee for the Course, £4 4s.

2. Inorganic Chemistry.—First year Honours Course, Non-metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Inorganic Chemistry.—Second year Honours Course, Metals. Tuesday, Thursday, and Saturday at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 11.30 p.m. Fee £3 13s. 6d.

5. Organic Chemistry Honours Course.—Wednesday and Friday at 9.30 a.m. Fee, £2 12s. 6d.

6. Theoretical Chemistry.—Advanced Course. Tuesdays and Thursdays at 9.30 a.m. Fee, £2 12s. 6d.

7. Chemistry as Applied to Coal Mining.—Tuesday during the First Term, at 4 p.m.

8. Agricultural Chemistry.—Monday, Tuesday, and Friday, at 3 p.m., during first and second terms.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session.—Students working six days per week, £18 18s.; five, £16 16s.; four, £14 14s.; three, £12 12s.

Class in Practical Chemistry, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Chemistry for Medical Students.—Saturdays, from 10.30 to 12.30, from October to end of March.

Practical Course in Sanitary Chemistry.—On Tuesday and Thursday, from 2 to 5, from April to July.

Practical Organic Chemistry for Medical Students.—On Mondays, from 11 to 1, from April to July.

Evening Class.

A Course of twenty Lectures by Mr. Ingle, on the Elements of Inorganic Chemistry (the Non-Metals) will begin during the first and second Terms, on Wednesdays, at 7.30 p.m., beginning October 14. Fee, 10s. 6d.

Dyeing Department.

Professor.—J. J. Hummel, F.I.C.

Lecturer.—L. Liechti.

Assistant Lecturers.—W. M. Gardner and J. B. Shaw.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Lecturer.—H. R. Procter, F.I.C.

The full Course, which extends over a period of three years, is suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and is recommended to sons of tanners. The Course includes instruction in chemistry, engineering, microscopy, leather manufacture, and practical work in the Leather Industries Laboratory.

Agricultural Department.

Professor.—James Muir.

The full Course occupies two years, and includes instruction in chemistry, physics, botany, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Cavendish, Salt, Akroyd, Brown, Emsley, Craven, and Clothworkers' Scholarships, and the Leighton Trustees' Exhibition, and one of the new 1891 Exhibition Scholarships. The West Riding County Council Scholarships are tenable at the Yorkshire College.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor.—J. Campbell Brown, D.Sc.

Lecturer on Organic Chemistry.—C. A. Kohn, B.Sc., Ph.D.

Demonstrators and Assistant Lecturers.—C. A. Kohn, B.Sc., Ph.D., T. L. Bailey, Ph.D., and A. F. Fryer, B.Sc.

Assistant.—H. H. Froyseil.

The Session commences October 1st.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Course A.—Non-metals. Fee, £3 10s.

Course B.—Metals. Fee, £3.

Course C.—Organic Chemistry. Fee, £3.

Course D.—Physical Chemistry. One Term. Fee, £1.
Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Course F.—Technological Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) Copper, Iron, and Steel. (3) Lead, Silver and Gold, Aluminium, and other Metals. (4) Distillation of Coal and Tar Industries. (5) Fuel. (6) Chemistry Applied to Sanitation. (7) Technical Gas Analysis. (8) Spectroscopy.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances. (3) Special Revision Class. (4) Senior: Practical Organic (Advanced Medical Class). (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Adulterations of Drugs and of Food, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class: Course arranged to suit the requirements of the London University B.Sc. Examinations, Pass and Honours, and for Intermediate M.B. Honours.

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical work.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Two Terms, Six Months.	Three Terms One Session.
One day ..	£4	—	£8
Two days ..	6	—	10
Three days ..	8	—	12
Four days ..	9	12	15
Five days ..	10	14	18
Six days ..	—	—	20

Technological Curriculum.

Preliminary Year.—Chemistry, either the Elementary Course or Course A, according to the previous knowledge of the Student. Practical Classes 1 and 2. Mathematics, or Mechanics, or Physics. Engineering Drawing and Design (in this or one of the following years). French or German. Or the Course for the Preliminary Examination, Victoria University, may be taken.

First Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week; Practical Organic Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German; Intermediate B.Sc. Examination may be passed. Engineering, First Year Course, Autumn and Lent Terms.

Second Year.—Chemistry, Lecture Course on Organic Chemistry, C, Lecture Course E or D, Technological Chemistry, Course F. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc. Pass Degree may be taken.

Third Year.—Courses D and F; part of Course C. Any other Courses omitted in a previous year. Laboratory, five days per week. Students may finally choose a special subject either of research or of applied Chemistry. The Examination for the Associateship of the Institute of Chemistry of Great Britain and Ireland may be taken. Three years study after passing the Preliminary Examination of Victoria University are required for the B.Sc. Degree in the Honours School of Chemistry.

Evening Classes.

Lectures will be given on Metallurgy, on the Chemistry of Photography, and on Practical Chemistry with Exercises.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, and a Sheridan Muspratt Exhibition of £25 for one year, will be awarded in December, 1893, on an Examination in subjects which are included in the first two years of the above curriculum. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

The Prospectus containing full particulars may be obtained from the Registrar, University College, Liverpool.

LIVERPOOL COLLEGE OF CHEMISTRY.

Principal.—George Tate, Ph.D., F.I.C., F.C.S.

The Laboratories are open daily from 10 to 5, excepting Saturdays, when they close at 1 p.m. The course of instruction is adapted to the requirements of students of Chemistry as a science, and in its applications to chemical and metallurgical industries. The fee for a three years' course of study is eighty guineas, or per session of three months eight guineas.

Prospectuses, containing full particulars of the day and evening classes, may be had on application at the College.

DURHAM COLLEGE OF SCIENCE,
NEWCASTLE-ON-TYNE.

Professor of Chemistry.—P. Phillips Bedson, D.Sc., F.C.S.

Lecturer in Chemistry.—Saville Shaw, F.C.S.

Lecturer in Agricultural Chemistry.—R. Greig Smith, B.Sc. (Edin.), F.C.S.

Assistant Lecturer and Demonstrator.—F. C. Garrett, M.Sc. (Viñ.), F.C.S.

The Session will commence on September 26th, 1892.

1. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. A section of this Course will be devoted to an outline of Organic Chemistry. The class will meet on Mondays, Wednesdays, and Fridays, at 11.15 a.m., and will commence on Wednesday, October 5th. Fee, £3 10s. for the Session.

2. *Advanced Course.*—Inorganic Chemistry, Tuesdays and Fridays, 3 to 4 p.m., during Michaelmas and Epiphany Terms.

3. *Organic Chemistry.*—A Course of about ninety Lectures will be given throughout the Session, the subject of which will be Organic Chemistry, or the Chemistry of the Carbon Compounds. This class will meet on Tuesdays and Thursdays, at 11 a.m., and will commence on Thursday, October 6th. Fee, £3 10s. for the Session.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for each course, £2 2s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m., commencing October 10th. Fee, £1 1s.

Metallurgy and Assaying.—A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry-Assaying, and in the preparation and analysis of Alloys, &c. Fee as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

A Lecture Course in Agricultural Chemistry will be

given on Wednesdays and Fridays from 12 to 1. Fee, Two Guineas.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. **Laboratory Fees.**—Students working six days per week, £5 5s. per term; three days, £3 3s. per term, £8 8s. per session; two days, £2 2s. per term, £5 5s. per session; one day per week, £1 11s. 6d. per term, £3 3s. per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Physical Science. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the two following examinations:—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.

2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Physical Science.—Every candidate for the Associateship in Physical Science will be required to satisfy the examiners in three, at least, of the five subjects,—Mathematics, Physics, Chemistry, Geology, and Biology,—in an examination, to be held at the beginning of his second year.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 20th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students.

OWENS COLLEGE,

VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory.—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry.—W. H. Perkin, Ph.D., F.R.S.

Demonstrators and Assistant Lecturers.—George H. Bailey, D.Sc., Ph.D.; Arthur Harden, M.Sc., Ph.D.; P. J. Hartog, B.Sc.; and S. H. Davies, B.Sc.

Lecturer in Dyeing and Printing.—Ernest Bentz.

Assistant Lecturer in Metallurgy.—Gilbert J. Fowler, M.Sc.

The Session begins on October 4, 1892, and ends on June 23, 1893.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

General Chemistry.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, Fridays, 3.30 p.m., during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (Honours).—Mondays, Wednesdays, and Fridays, 9.30, during the Session.

History of Chemistry and Chemical Philosophy.—Wednesdays, 10.30, during the Session.

METALLURGY.—**Lectures:** The Metallurgy of Copper, Lead, Silver, Gold, and the Metallurgy of Iron and Steel will be given in alternate years. **Practical:** Saturdays, 9.30. The Chemical Laboratories are open daily from 9.30 a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

An ordinary degree of B.Sc. in Chemistry, Victoria University, may be taken at the College in three years. The Degree of B.Sc. with Honours in Chemistry can also be taken in three years, and the College Certificate in Technological Chemistry may be taken in the same time.

A number of important Scholarships, &c., are available to students.

Technological Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—The Chemistry of Coal Tar.

Fourth Course.—Natural and Artificial Dye-stuffs.

Fifth Course.—Calico-printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Honours Course on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

A combined Lecture and Laboratory Course on the Bleaching, Dyeing, and Printing of Cotton Fabrics is given on Saturdays, at 3, by Mr. Bentz.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENT OF CHEMISTRY, METALLURGY, AND AGRICULTURE.

Professor of Chemistry.—Frank Clowes, D.Sc. Lond., F.I.C.

Demonstrators of Chemistry.—J. B. Coleman, A.R.C.Sc. Dublin, F.I.C., and R. L. Whiteley, F.I.C.

Lecturers.—J. B. Coleman, F.I.C.; R. L. Whiteley, F.I.C.; C. Haydon White, M.R.C.S.; J. W. Carr, M.A.; F. R. Sargeant; and M. J. R. Dunstan, M.A., F.R.S.E.

The Classes of the College are open to students of both sexes above sixteen years of age.

The dates of commencement and end of Terms in the Session 1892-93 will be as follows:—First Term, October 10th to December 24th; Second Term, January 16th to March 30th; Third Term, April 17th to July 1st.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Non-Metals for the first two terms and for Elementary Organic Chemistry in the third term. In his second year he takes the course on Metals for the first two terms, and Advanced Organic Chemistry. In his third year he attends a course on Applied Chemistry during the first two terms. Fee for Day Lectures and Classes: Non-Metals or Metals 42s.; Organic Chemistry (one term) 21s.; Applied Chemistry, 30s.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 2s. 6d.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry.—The chemical laboratory is open every day except Saturday and Thursday from 10 to 5, on Thursday from 10 to 1, on Saturday from 10 to 12, and on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation and in Qualitative and Quantitative Analysis; and students are enabled to work out the applications of Chemistry to Pharmacy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees: For one term, £7; for the session, £18; for day students for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for one evening per week, and 20s. for two evenings per week, per term.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

A **Pharmaceutical Curriculum** extending over three Winter Sessions, includes Pharmaceutical Chemistry (lectures and laboratory work), Pharmaceutical Botany (lectures and class work on specimens), Materia Medica (lectures and use of specimens), Practical Dispensing, taught by demonstrations and practical work in the laboratory, and Lecture and Laboratory Instruction in Physics.

Government Lectures and Classes.—Evening Lectures and Laboratory instruction will be given by the Demonstrators of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry, agricultural chemistry, and metallurgy will be taught in the elementary, advanced, and honours stages, each of which commences at the beginning of the College Session in October. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

An **Agricultural Course** of instruction, extending over two years, is now organised under the general direction of Mr. M. J. R. Dunstan, M.A., F.R.S.E. It includes instruction in chemistry, botany, agriculture, with practical work on experimental fields, dairy work, farriery, land

surveying, &c. The instruction is designed for those who intend to become farmers, bailiffs, land agents, or colonists, and may be extended to a third year if desired. Fee, £15 per annum for residents in Notts, £20 to residents in other counties.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

FIRTH COLLEGE, SHEFFIELD.

Professor of Chemistry.—W. Carleton Williams, B.Sc. F.C.S.

Demonstrators and Assistant Lecturers.—L. T. O'Shea, B.Sc., F.C.S., and G. Young, Ph.D.

The Session will commence on October 1st.

First Year's Course.—Chemistry of the Non-Metallic Elements. Monday, Wednesday, Thursday, from 10 to 11 a.m. Fee, £3 3s.

Second Year's Course.—Chemistry of Metals. Tuesday, Wednesday, and Thursday, from 10 to 11 a.m. £3 3s.; or for the First and Second Courses, £5 5s.

Third Year's Course.—Organic Chemistry, on Wednesday, from 9 to 10, and Saturday, from 10 to 11. Fee, £2 2s.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.; Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Students who have worked for three sessions in the Chemical Laboratory are eligible for election to a scholarship value £150 for two years.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9, and another series to be arranged if desired. Sessional Fee, one evening per week, £1 10s.; two, 50s.; or Lecture Class and Laboratory, on Wednesday evening, £1 10s.

UNIVERSITY COLLEGE, DUNDEE.

(UNIVERSITY OF ST. ANDREWS).

Professor.—Percy F. Frankland, Ph.D., B.Sc., F.R.S., &c.

Assistant Lecturers and Demonstrators.—F. J. Hambly, F.C.S., and J. R. Appleyard, F.C.S.

The tenth session of the College will be opened on October 18th, 1892.

The Lectures and Laboratory practice in this University are recognised by the Royal College of Physicians and Royal College of Surgeons, London, and by the Royal College of Surgeons, Edinburgh, and for degrees in Science and Medicine by the Universities of Edinburgh, Glasgow, and Aberdeen.

The courses are suitable for the Degrees of the London University and for the Civil Service appointments, and will also satisfy the requirements of students in Pharmacy, and of students who intend to become candidates for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

Lecture Courses.

The object of these courses will be (1) to give systematic instruction in the general principles of the science, and information regarding the elements and their more important compounds; (2) to show how this knowledge may be usefully applied in the Arts and Manufactures.

A course of instruction in Practical Chemistry in the Laboratory is recommended to all who wish to obtain a sound knowledge of the science, and the methods of applying it to useful purposes—the duration of such course depending upon the special wants of the student.—The Professor will be glad to give any information to intending students.

First year's lecture course: General Chemistry (Non-Metals, Metals, and Elements of Organic Chemistry) (100 lectures), Monday, Tuesday, Wednesday, Thursday, and Friday, from 10 to 11 a.m.; fee, £3 3s.

Second year's lecture course: 1. Advanced Inorganic Chemistry, including modern Chemical Theory (50 lectures). 2. Organic Chemistry (50 lectures). Fee for the whole course, £3 3s.

A Lecture Course on Analytical Chemistry will be given on Saturdays, from 9 to 10. Fee, £1 rs.

Courses of lectures will be given on Dyeing, Bleaching, and the Chemistry of the Textile Fibres, with practical instruction in the Laboratory and Dyehouse. In connection with this Department there is an extensive Technical Museum, containing a large collection of specimens illustrating many branches of Applied Chemistry, and particularly the local industries.

Practical Chemistry (Laboratory).

The aim of the Laboratory Courses is to make the student practically acquainted with the science, so that he may conduct chemical analysis and original research, and generally to fit him for applying the science to the Arts, Manufactures, Agriculture, and Public Health. The courses are also arranged for students preparing for their medical and pharmaceutical examinations. A three months' course of practical instruction in Sanitary Chemistry for the B.Sc. Edinburgh, in the department of Public Health, may be taken in the College Laboratory.

The Laboratory will be open for students daily from 9 a.m. to 4 p.m., except on Saturdays, when it will be closed at 2 p.m. Each student on entering will be allowed to arrange his working hours to suit his own convenience, but will be required to keep the hours when once fixed.

Sessional Fees for Day Students:—The fees for both sessions are—for six hours per week, £3 3s.; each additional hour per week, 10s. 6d. Day students may not enter for less than six hours a week. Students joining the Laboratory during the second term will be charged two-thirds, and during the third term one-third of the above fees. Students may also enter for short periods, working every day in the week at the following fees:—For one month, £2 12s. 6d.; for two months, £5 5s.; for three months, £7 7s.

Evening Classes.—Courses of Lectures and Practical Laboratory instruction are given in Chemistry, Dyeing, and Bleaching.

Forster Research Scholarship.

This scholarship, of the value of £30, is awarded annually to the best student on the condition that he devotes himself during the ensuing year to original research in the College Laboratory.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor.—Alex. Crum Brown, M.D., D.Sc., F.R.S., Pres. C.S.

Assistants.—J. Gibson, Ph.D.; L. Dobbin, Ph.D.; H. Marshall, D.Sc.; J. Walker, Ph.D., D.Sc.; Theodore Rettie, B.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to end of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. A class for advanced students is held in summer: it meets thrice weekly; fee £2 2s.

In addition to the above, Lecture Courses are given by the Assistants on special subjects, such as Chemical Theory, Physical Chemistry, or some particular branch of Organic and Inorganic Chemistry. These lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

Laboratories.—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 10 till 4. (Fees: Winter Session, £10 10s.; Summer Session, £6 6s.) Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. (In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy and Chemistry. The Second B.Sc. Examination includes any three or more of the following subjects:—1. Mathematics. 2. Natural Philosophy. 3. Astronomy. 4. Chemistry. 5. Human Anatomy, including Anthropology. 6. Physiology. 7. Geology, including Mineralogy. 8. Zoology, including Comparative Anatomy. 9. Botany, including Vegetable Physiology. Chemistry in this examination includes Inorganic Chemistry, Organic Chemistry, Relation between Chemical and Physical Properties, Complex Qualitative Analysis (practical), and Simple Quantitative Determinations (practical).

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Professor.—W. H. Perkin, Jun., Ph.D., F.R.S.

Assistant Professor.—Arthur W. Bishop, Ph.D.

Demonstrator.—Bertram Prentice.

The Session begins October 1st, 1891.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Lecture Course to day students in Chemistry is at present mainly devoted to Inorganic Chemistry. In the Laboratory course each student is required to prepare and

study the properties of the principal elementary and compound gases; to perform the more important experiments shown by the Professor in the Lecture Room; to make himself thoroughly acquainted with the preparation and purification of salts, and with the tests employed in identifying these. After a careful study of the reactions of the principal metals and acids, he passes on to a complete course of the systematic qualitative analysis of simple salts and mixtures, and may then, if attending a second year, take up an extensive course of quantitative analysis (gravimetric and volumetric), ultimately making a speciality of any branch of the subject which may be most necessary for his future work. Great attention has been paid to the thorough equipment of the Advanced Laboratories, and special facilities are given to students who may wish to engage in any class of Research (Inorganic or Organic) whether of a purely Chemical or of a Technical nature.

The teaching in the Evening Classes is based on the Syllabus of the Science and Art Department, and includes Elementary, Advanced, and Honours Courses in Theoretical and Practical Inorganic and Organic Chemistry.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following any industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Copies of the Calendar for 1892-93 may be had from Mr. John Young, B.Sc., the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

Professor of Chemistry.—T. Purdie, B.Sc., Ph.D., Assoc. R.S.M.

The Session begins on October 18th. A Competitive Examination, open to intending Students of Arts or Science, for a number of Entrance Bursaries, ranging in value from £40 to £10 each per annum, will be held on the 13th, 14th, and 15th of October. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment. The Lectures are supplemented by a Course of Laboratory Practice of two hours per week, to which Members of the Class are admitted without additional fee.

These courses of instruction are intended to meet the requirements of the Arts' Curriculum; also of candidates for the First B.Sc. Examination, and of students of medicine, so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part treats of the more advanced General Principle and Theory of Chemistry, the instruction in general being such as is required for the Second B.Sc. Examination.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £13 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the First and Second B.Sc. Examinations, and for Students of Medicine.

The fees for Practical Chemistry vary according to the number of hours taken weekly.

QUEEN'S COLLEGE, BELFAST.

Professor.—E. A. Letts, Ph.D., F.R.S.E., F.C.S.

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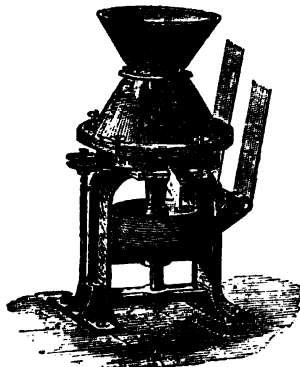
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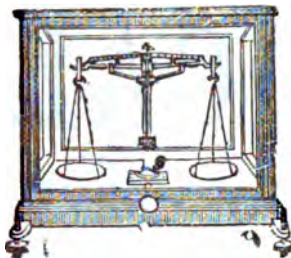
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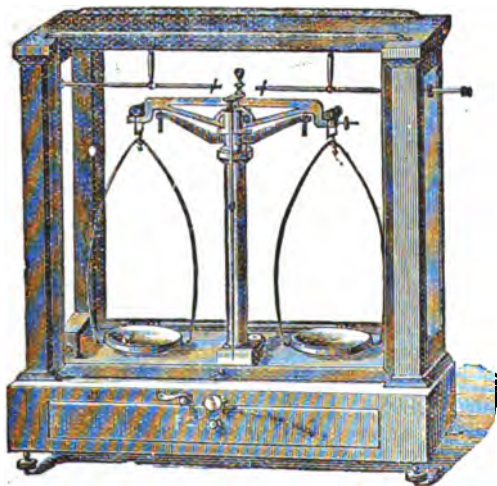


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THE CHEMICAL NEWS.

VOL. LXVI., No. 1712.

EXPERIMENTS ON FLAME.*

By ARTHUR SMITHELLS, B.Sc.

THE author began by describing four distinct regions of an ordinary luminous flame, the existence of which he thought could not be denied by any impartial observer. His experiments had arisen from a desire to understand more fully the chemical changes which determined this peculiar structure, and especially the twofold character of the outer sheath. He described the construction and demonstrated the use of his apparatus for separating the two cones of combustion in non-luminous flames, and gave a summary of the results he had obtained with it. He considered these results to furnish fresh proof that when a hydrocarbon is starved of oxygen the carbon will burn more readily than the hydrogen, and that accordingly the luminosity of ordinary flames must not be explained, as is often done, by assuming the very reverse of this. The luminosity of ordinary flames is now generally admitted to be due to the separation of solid carbon in the flame, and this must be ascribed to a decomposition or dissociation of the hydrocarbons by heat. This heat is supplied by the sheath of non-luminous combustion surrounding the flame. The author considers this sheath, which consists of two parts (a barely visible outer part and a bright blue inner one), to correspond to the two cones of combustion in a non-luminous flame. The author, whilst admitting from the result of experiments made by Prof. Lewes and by himself that acetylene was present in the interior of luminous flames, thought that Prof. Lewes had not established his view that luminosity was mainly and essentially due to the formation and subsequent dissociation of acetylene, and that he was altogether relying too much upon that substance. A study of the precise cause of carbon separation was being undertaken by the author with the aid of his flame-cone separator, a single hydrocarbon (ethylene) being employed. Other experiments with the flame-cone separator relating to the spectra of metallic salts were exhibited. The chief conclusion was that the spectra obtained when metallic salts were introduced into non-luminous flames were the outcome of and were dependent upon chemical changes.

Sir GEORGE STOKES, referring to the latter portion of Prof. Smithells' paper, said he believed that he was to some extent in agreement with the author, but that there was one point of difference. He accepted the view that spectra obtained in flames may be due in an important degree to the heat developed during the chemical reaction. He was of opinion, however, that the particular radiations produced must be ascribed not to the act of combination, but to the consequences of that act in setting up a vibration of the newly formed substance. He attributed the phenomena, in fact, to the child of the reaction and not to the parents. He had explained his views on the subject to Prof. Smithells in the course of correspondence, and he would only now say that he found insuperable difficulty in ascribing the absorption spectrum of sodium to chemical action.

With reference to the luminosity of flames he considered it established beyond question that this was due to solid matter. He described the optical proof which he and

others had adduced. He understood from Professor E. Frankland that the latter had abandoned the view that luminosity was due to dense hydrocarbon vapours.

Sir HENRY ROSCOE agreed with Sir George Stokes that there would be great difficulty in explaining absorption spectra on the hypothesis put forward. He was, however, of opinion that it was not unnatural to ascribe some effect to the disengagement of heat during chemical reactions, and he thought that it would be difficult if not impossible to explain some of the experiments which had been shown on any other assumption.

Mr. THOMAS alluded to the experiments which he had performed a good many years ago on the combustion of hydrocarbons with restricted amounts of oxygen during a study of fire-damp explosions. He had shown that carbonic oxide and free hydrogen were produced in such cases, but he was inclined to ascribe this not to the prior combustion of the carbon but to the combustion of part of the gas to carbon dioxide and water, and the subsequent action of those substances on the residual hydrocarbon.

Prof. LIVING expressed general concurrence with the view that chemical action had an effect in the production of spectra, and he alluded to some unpublished experiments by Prof. Dewar and himself on the absorption spectrum of liquid oxygen, in which phenomena were observed that he could only ascribe to the action of oxygen molecules on each other. With regard to the luminosity of flames he thought that Prof. Frankland had no need to abandon the view that it might be due to hydrocarbons, though undoubtedly the hydrocarbons were solid in the flames. He, the speaker, had found it impossible by any process to deprive carbon separated from flames, of the hydrogen which it always contained, and which he therefore thought to be in a state of chemical combination with the carbon.

Prof. RAMSAY said he agreed with Prof. Smithells up to the hilt. He had lately found that with perfectly pure sodium in a vacuum tube it was impossible to get any trace of the D line.

Prof. LEWES, in reply to the discussion, said that he felt sure of the facts that he had stated with respect to acetylene, but did not consider the subject worked out. He quite agreed with Prof. Smithells as to the impossibility of making exact analyses of mixtures of hydrocarbons, but acetylene was one of the few that could be determined with precision. He did not agree that a doubt of the readier combustibility of carbon than hydrogen was mere prejudice, and he thought that so long as the chemical changes taking place could be explained on the older views, it was unnecessary and undesirable to bring forward the theory advocated by Prof. Smithells. He was sorry if he had misrepresented Prof. Frankland's views, but he had certainly understood from that gentleman that he still adhered to his theory of luminosity being due to dense hydrocarbon vapours.

Prof. SMITHELLS, in reply, wished to clear himself of a suspicion of having brought forward revolutionary and unnecessary theories. As a matter of fact the theory he advocated, that the carbon of a hydrocarbon burnt more readily than the hydrogen, was put forth at the beginning of the century by John Dalton. Dalton's discovery had been ignored until the same facts were again discovered by Kersten. Even that was not enough to secure their acceptance by the text-book makers, and though the matter had again been independently brought to light by Ernst von Meyer and Thomas, he (the speaker) had once more to discover it, and endeavour to put it forward in place of what Prof. Lewes called the orthodox idea, but what was really an idea that had been exploded at the beginning of the century.

Mr. P. J. HARTOG remarked that a crucial experiment had been performed in Prof. Dixon's laboratory. The rate of explosion of ethylene with sufficient oxygen to produce carbonic oxide had been measured, and it had been found that if the oxygen were increased beyond this

* Read before the British Association, Edinburgh Meeting, 1892, Chemical Section. The Paper of which this is an abstract and the discussion followed the Paper read by Prof. Vivian Lewes and published in the CHEMICAL NEWS, vol. LXVI., p. 99.

the velocity of explosion was diminished, the extra oxygen acting merely as a diluent. This clearly proved that the carbon first burnt to carbonic oxide.

Prof. LEWES said this was the first fact that he had heard which appeared to him in any degree of a decisive character in favour of the readier combustibility of carbon.

The PRESIDENT conveyed the thanks of the meeting to the readers of the papers.

NOTE ON

SOME ALLOYS OF IRON, ALUMINIUM, AND MANGANESE.*

By T. W. HOGG.

THE alloys which form the subject of this short paper were prepared by mixing ferro-manganese with aluminium, both previously fused. These alloys possess the unexpected feature of being readily attracted by the magnet, and it is principally on this account that they have been thought sufficiently interesting to bring before the members of this section, especially as the alloys of aluminium have for some time been attracting much attention.

It is now well known that the addition of manganese to iron or steel produces an alloy which is not attracted by the magnet, alloys containing 8—12 per cent of manganese being only feebly magnetic, and over this proportion they may be said to practically have no influence on the magnet at all.

Aluminium also possesses a similar property, but in a less marked degree. Ferro-aluminium containing 13 per cent Al is still readily attracted, and it is not until the alloy contains about 20 per cent Al that the effect here alluded to takes place.

It is therefore an interesting fact that the addition of aluminium to a ferro-manganese alloy, which of itself would be quite inert, becomes readily attracted. In one of the alloys here shown the aluminium is only present to the extent of 3.05 per cent, and although it contains only 14.80 per cent iron, it responds to the influence of the magnet almost as readily as a piece of iron.

With regard to the disintegrated alloy the effect is still more remarkable, as we have present not only manganese but also a sufficient quantity of aluminium itself to destroy the influence of the magnet; yet instead of acting together in the same direction they have done exactly the reverse, and here again, although the proportion of iron is small, the magnet attracts it readily.

The alloys which I have here alluded to were the result of an experiment made to ascertain the possibility of forming a reliable homogeneous alloy of aluminium with ferro-manganese, and for this purpose 50 lbs. of ferro-manganese containing 82 per cent Mn, and 5.56 lbs. of aluminium containing 99.5 per cent Al, were separately melted in large crucibles. After perfect fusion the ferro-manganese was poured into the aluminium; after stirring for about half a minute the mixture showed such decided signs of becoming pasty that it was at once poured into an ingot mould. After about two-thirds had been poured the remainder suddenly solidified and was roughly knocked out of the crucible. The alloys presented no apparent dissimilarity, and it was not thought worth while to examine them until after keeping for about three months, when the portion which had solidified in the crucible commenced to fall into pieces in the same way that high percentage ferro-manganese (85 per cent Mn) is known to do, and this action has gone on until after twelve months it has completely disintegrated and is now in the condition of the specimen shown.

The analyses of the two portions showed a remarkable

difference in composition. The disintegrated portion contains:—

Iron	10.80
Manganese	54.86
Carbon	2.32
Aluminium	25.34
Silicon	0.79
Sulphur	traces
Phosphorus	0.107
Copper	0.075

94.292

This analysis was repeated with practically the same results; the deficiency is no doubt due to oxygen, slight oxidation having taken place owing to the finely-divided condition of the alloy. It has a specific gravity of 3.61.

The examination of the portion which was poured off showed it to have a specific gravity of 6.12, and that it contained:—

Iron	14.80
Manganese	75.40
Carbon	5.55
Aluminium	3.05
Silicon	0.886
Sulphur	traces
Phosphorus	0.184
Copper	0.075

99.945

This alloy has not altered its condition since it was made, there being no signs of disintegration. Whether this difference in composition between the two alloys is the result of the great difficulty of mixing aluminium with the heavier metals, or has been produced by separation, is not quite clear, if the carbon may be taken as an indication; it seems to show not only separation but also actual loss of this element.

A QUICK METHOD FOR REFINING GOLD, SILVER, AND PLATINUM IN QUANTITY.

By H. N. WARREN, Research Analyst.

THE following note refers principally to the refining of standard silver, gold, and dental alloy, or other such commercial metalliferous products containing the precious metals. It not infrequently happens that in assay offices where these metals are purchased in large quantities that before rendering them fit for the market a separation of each is required. The gold alloys are in this case melted and further alloyed with two and a half times their weight of standard silver, the alloy thus obtained parted by the aid of nitric acid, the amorphous gold remaining dried, after washing, and granulated. The solution containing the silver as nitrate freed from the same by the introduction of copper bars, the precipitated silver washed, dried, and melted, being either cast into bars or granulated as required, the copper being afterwards replaced by iron in order to serve for a further operation.

Dental alloy—that is, silver alloyed with from 25 to 30 per cent of platinum—presents a more difficult problem. Platinum alloyed with a sufficiency of silver is soluble in nitric acid; but in this case about 10 per cent of that metal passes into solution after long boiling with the same, the whole of the silver in the meantime becoming dissolved. To the solution containing the platinum as nitrate is introduced also a bar of copper; the whole of the platinum, together with the silver, are thus quickly replaced, the silver being afterwards re-dissolved by the addition of a further quantity of nitric acid, leaving the platinum untouched, which is now returned to the first portion, and the whole dissolved by the addition of *agua*

* Read before the British Association, Edinburgh Meeting, 1892, Section B.

regia, precipitated by an excess of ammonium chloride, evaporated to dryness, and ignited, leaving pure platinum.

The precipitation of silver as chloride in presence of platinum is useless, as it carries down with it nearly a quarter of the platinum present.

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DISCOVERY OF HEXA-iodo-BENZENE.

By G. E. SHAW.

In attempting to prepare *p*-di-iodo-benzene by Ystrati's method (*Bull. Chem. Soc.* [3], v., p. 158), 250 grms. iodine were heated with 100 c.c. pure benzene and 200 c.c. strong HSO_4 a few hours daily for ten days. A mixture was obtained from which, besides mono- and di-iodo-benzene, another compound was easily separated by its comparative insolubility in alcohol and benzene. By crystallisation from CS_2 , after treatment with animal charcoal, about 20 grms. were obtained in white needles containing only C and I. Two estimations of the iodine gave (1) 89.99 per cent, (2) 91.10 per cent; agreeing with the formula C_6I_6 , 91.33 per cent I. Its melting-point (corrected) is 248°C . Aniline and nitrobenzene are the only solvents in which it freely dissolves. Baeyer (*Ber.*, xviii., p. 2275), obtained a white substance soluble in alcohol and melting at 184°C . by heating di-iodo-acetylene on a water-bath, and which he supposed to be C_6I_6 , but gives no analysis. If hexa-iodo-benzene was really formed at all it must have been very impure.

Finabury Technical College, Aug. 23, 1892.

ON THE DISSOCIATION OF ELECTROLYTES IN SOLUTION AS SHOWN BY COLORIMETRIC DETERMINATIONS.

By H. M. VERNON, B.A.

(Continued from p. 115).

The Influence of Temperature on the Colour Effects of Salt Solutions.

In addition to determining the effects of dilution on salt solutions, the effect of temperature was also tried. Generally, 30 c.c. of the solution was taken, and this was first compared, merely as a test for the correctness of colour judgment, with some of the solution of the same concentration, both solutions being at 20°C . The value found generally agreed to within 0.5 c.c. The tube containing the solution was then placed in a water-bath and heated to from 62° to 63° . It was then compared as to colour with the original solution, the radiation between the two tubes being stopped by placing a thick piece of cardboard between them. The short time necessary for the comparison was just enough for the solution to cool to 60° , or to within half a degree of this temperature. The temperature of the solution was again taken immediately after the comparison had been made to verify this. The solution was then allowed to cool to 52° , when it was again compared, then to about 41° , then to a little above 30° , and lastly it was compared again at 20° in case any change may have taken place in the solution caused by the heating, as was found to be the case with one or two ferric salts. It was scarcely possible to make comparisons at temperatures much above 60° , as the solution then began to give off enough aqueous vapour from its surface to produce a cloudiness in the tube.

Salt.	Dilution in litres.	Colouration at—			
		30° .	40° .	50° .	60° .
Cupric sulphate ..	1	102.6	106.1	111.3	116.5
" " ..	10	104.7	109.1	112.5	115.7
" " ..	100	104.9	106.2	110.6	113.8
" chloride ..	0.4	112.5	118.3	123.3	—
" " ..	10	104.1	106.7	109.5	113.6
" " ..	100	105.4	110.1	113.1	117.1
" nitrate ..	1	102.3	104.6	105.9	108.2
" " ..	10	103.4	107.5	110.6	112.2
" chlorate ..	1	101.8	103.7	106.7	109.8
" " ..	10	105.9	112.5	115.6	119.5
" acetate ..	2.5	107.2	122.9	133.1	145.2
" " ..	10	109.8	119.1	128.6	138.7
" " ..	100	105.3	117.1	122.1	129.2
Nickel sulphate ..	1	101.9	106.2	107.5	108.7
" " ..	10	101.9	106.2	108.5	111.8
" chloride ..	1	104.7	108.5	115.6	122.7
" " ..	10	101.6	105.8	114.8	118.8
" nitrate ..	1	102.4	104.9	108.5	—
" " ..	10	103.7	105.4	108.4	113.9
Cobalt sulphate ..	1	105.0	114.3	126.1	141.2
" " ..	10	109.7	117.4	130.3	—
" " ..	100	103.9	107.9	116.8	—
" chloride ..	1	113.9	122.6	136.5	142.6
" " ..	10	107.7	111.9	117.3	125.0
" " ..	100	105.8	108.1	113.0	116.6
" nitrate ..	1	111.5	128.3	143.3	170.0
" " ..	10	105.7	110.1	118.0	126.3
" " ..	100	102.1	103.7	106.7	110.7
Uranyl sulphate ..	2.5	103.5	108.7	113.0	120.9
" " ..	10	106.5	116.2	123.1	131.3
" " ..	100	102.8	108.7	115.7	121.6
" chloride ..	2.5	112.3	122.9	133.6	145.1
" " ..	10	105.3	113.9	129.1	137.5
" " ..	100	106.6	113.7	117.5	124.6
" nitrate ..	2.5	111.1	122.2	134.2	139.3
" " ..	10	104.1	111.3	118.5	122.3
" " ..	100	105.5	111.5	116.9	121.4
" acetate ..	2.5	106.4	113.7	121.7	134.6
" " ..	10	104.0	108.6	116.9	121.3
Chromium sulphate	10	—	—	—	100
Chrome alum ..	10	113.4	123.2	134.8	142.0
Chromium chloride	10	—	—	—	100
" nitrate ..	10	—	—	—	100
Potassium chromate	1	127.1	162.0	188.5	204.8
" " ..	10	115.0	148.1	187.3	237.7
" " ..	100	110.1	116.0	132.1	146.8
" bichromate	10	103.2	105.5	113.6	121.5
" " ..	10	118.7	137.1	151.2	164.9
" " ..	100	106.1	116.8	129.1	143.1
" " ..	1000	105.1	115.6	122.0	—
Chromium trioxide	1	111.6	128.5	150.6	176.6
" " ..	10	108.3	124.8	141.0	151.6
" " ..	100	104.6	108.8	118.9	125.9
" " ..	1000	100	100	100	100
Ferric chloride ..	1	116.4	134.8	154.0	171.1
" " ..	10	127.9	155.9	200.1	248.9
" " + HCl	1	136.4	188.3	236.0	256.9
" " ..	10	174.7	286.4	—	—
" acetate ..	10	105.3	117.1	122.4	130.3
" oxalate ..	5	107.7	114.2	126.9	140.4
" " ..	100	124.4	145.4	175.2	199.6
" tartrate ..	10	112.9	125.4	140.2	168.7
" " ..	100	117.6	126.5	150.2	—
" citrate ..	5	112.8	123.8	134.9	157.5
" " ..	100	104.2	109.6	112.3	125.1
Ferric citrate + citric acid ..	10	105.7	112.3	120.7	129.5
Ferric citrate + citric acid ..	100	106.9	119.0	129.7	141.7
Ferric citrate + citric acid ..	1000	102.1	104.0	105.7	110.7
Ferric ammonium citrate ..	100	—	—	—	103.3

Salt.	Dilution in litres.	Colouration at—			
		30°.	40°.	50°.	60°.
Ferric ammonium citrate	1000	104'1	105'1	107'6	108'3
Ferrous citrate	100	111'6	115'4	119'8	124'5
Potassium ferrocyanide	1	108'2	116'4	127'6	139'4
Potassium ferrocyanide	10	103'8	107'6	113'3	123'2
Potassium ferridcyanide	1	—	—	—	106'0
Potassium ferridcyanide	10	—	—	—	105'1
Potassium ferridcyanide	100	—	—	—	103'6
Potassium permanganate	1000	—	—	—	103'3
Potassium permanganate	10000	—	—	—	100
Iodine	100	—	—	—	100

Of copper salts, the sulphate shows a moderate increase of colour with rise of temperature, the increase being about the same for the normal and decinormal solutions, and slightly less for the centinormal. Cupric chloride shows about twice as great an increase in its most concentrated solution as the sulphate does, but in the decinormal and centinormal solutions it falls to about the same value. The cupric chloride solutions were very difficult to compare accurately, as they change colour so greatly on heating. Thus no colour comparisons could be made with the normal solution, as it is blue at 20°, but quite green at 50° or 60°. Cupric nitrate solutions show less increase in colour on heating than any other cupric salts. The normal cupric chlorate solution comes next. In both cases, but especially with the chlorate, the 10 litres solution shows considerably greater increase than the normal solution. Solutions of cupric acetate show greater increase in colour than any other copper salts, the 2.5 litres solutions showing the greatest increase, then the 10 litres, and then the 100 litres solution. Nickel salts show a similar increase to the copper salts, the chloride showing the most increase, and the sulphate and nitrate possessing almost identical values. With all the nickel salts at all dilutions, the solutions were considerably more yellowish in tinge at the higher temperatures than at the lower. Cobalt salts show considerably greater increase on rise of temperature than either copper or nickel salts. With the 10 litres and 100 litres solutions of the sulphate, colour comparisons could not be made at 60°, as a slight decomposition set in, and they became milky. Like the solutions of the chlorides of copper and nickel, that of cobalt shows a much greater increase for the 1 litre solution than for the 10 litres, while this again is greater than for the 100 litres solution. The nitrate of cobalt shows a similar behaviour, only to a more marked extent. Cobalt nitrate acts quite differently from the nitrates of either copper or nickel. All the cobalt solutions were more purple in tinge in the hot solutions than in the cold; this was especially the case with the nitrate.

Uranyl salt solutions, taken as a whole, show considerably greater increase in colour effect on heating than those of either copper or nickel salts, their values, in fact, approaching to those of cobalt salts. Unlike these salts, however, there is not nearly so great a difference between the values or the solutions of different concentrations. The chloride, like cupric, nickel, and cobalt chlorides, shows the greatest increase in its concentrated solution and the least increase in its most dilute. The nitrate also acts in the same way. It will thus be seen that, in respect of the relation of increase in colour to temperature, the uranyl salts show great resemblance to the corresponding cobalt salts.

Chromium salts, with the exception of chrome alum, act in a different manner from almost all other salts, for

they show no change of colour whatever on rise of temperature. To what this is due it is not possible to say, but it is remarkable that these salts and potassium permanganate, which likewise is scarcely at all affected by temperature, all crystallise without water of crystallisation, whilst chrome alum, whose crystals contain water of crystallisation, is affected by temperature like other salts. Also, it is doubtful whether solutions of chromium salts, except chrome alum, undergo any true decrease of colour at all on dilution, and potassium permanganate only undergoes a slight decrease at extreme dilutions. The values given for chrome alum are scarcely even approximate, as the solution becomes so green on rise of temperature that accurate comparison is impossible. At 100° chrome alum solutions become as green as chromium sulphate solutions; it can thus at this temperature contain no molecules of chrome alum as such in solution, but only chromium sulphate molecules. The change of colour was still more marked with the 100 litres solution, so that in this case no comparison could be made at all.

Potassium chromate, though crystallising without water of crystallisation, and though showing no decrease in colour whatever on dilution of its solutions, is nevertheless more affected by temperature in its solutions than almost any other salt examined. Its decinormal solution shows the greatest increase, and its millinormal the least. The same thing holds for potassium bichromate. The dependence of the amount of colour change of a salt solution on the dilution is most strikingly displayed in the case of chromium trioxide; for whilst the colour of the normal solution is almost doubled on heating to 60°, that of the millinormal undergoes no change whatever. This latter solution therefore contains the salt in such a state that it has less than half the colour effect of the concentrated solution, and is also wholly unaffected by temperature. As has been previously shown, this solution probably only contains H_2CrO_4 molecules, so the dilution must be so great that even a considerable rise of temperature is not enough to set free any molecules of CrO_3 , and so cause an increase in colour.

Ferric chloride solutions are greatly affected by temperature—the decinormal solution more than the normal. This is due to the formation of ferric oxide in the solution, for on heating the centinormal solution to 60°, it became dark reddish brown, and moreover did not regain its original colour on cooling to 20° again.

Solutions of ferric chloride containing free hydrochloric acid are much more affected by temperature than solutions of ferric chloride alone. The great increase in colour is not due to the same cause however. It has been shown how largely acid ferric chloride solution dissociates on dilution, and it was also remarked how very greatly the colour of the normal solution is changed on dilution to 5 litres, the change being from brown to yellow. Now on heating the acid ferric chloride solutions, they also change very rapidly to a more brownish colour, so much so that no colour comparisons could be made with the decinormal solution above 40°. It is clear, therefore, that on heating a solution the salt tends to change to the same condition in which it exists in its more concentrated solutions at ordinary temperatures. As, therefore, on concentrating acid ferric chloride solutions from 100 litres to 1 litre, the colour is increased to more than six times its value, the increase of colour from 100 to 256.9 on heating to 60° is not extraordinary.

Decinormal ferric acetate solution shows a moderate increase of colour on heating. More dilute solutions than this could not be examined, as they decomposed with the formation of the basic acetate. Ferric oxalate solutions showed a greater increase, especially the 100 litre solution, the colour effect of which was doubled by heating to 60°. This was evidently owing to the same cause that affected acid ferric chloride solutions, for concentrated solutions of ferric oxalate are of a yellowish brown colour, and dilute solutions of a dirty green, and these solutions, with rise of temperature, rapidly begin to turn

brownish yellow, and so the molecules of the salt in them must exist in the same state as in the more concentrated solutions.

Ferric tartrate solution showed about the same colour increase as the oxalate solution. The value for the centinormal solution could not be determined at 60°, as the salt began to decompose and the solution turned milky. Ferric citrate and acid ferric citrate solutions show similar values. Ferric ammonium sulphate solutions on heating show only a very slight increase of colour effect, and, as has been shown, this salt undergoes no change in colour on dilution, whilst ferric citrate solutions increase considerably in colour. Ferrous citrate solution shows a moderate increase in colour on heating.

The normal solution of potassium ferrocyanide shows considerably greater increase in colour than the decinormal. It would be thought that the increase for potassium ferridcyanide would, if anything, be greater than that of the ferrocyanide, but such is not the case. Potassium permanganate shows a barely perceptible increase at 1000 litres dilution, whilst at 10,000 litres it shows no change at all. Iodine solution, which exhibited such remarkable variations in colour on dilution, did not on heating show any change at all. In this respect it resembles chromium salts.

The effects of temperature on solutions of different coloured salts have thus been examined in detail; it remains for us to draw a few general conclusions from the results. In the first place it is evident that all the salt solutions may be divided into two classes, one containing solutions which increase in colour on rise of temperature; this class includes almost all the solutions examined, and the other class containing those salts which show no change of colour. There is no third class containing solutions which decrease in colour on heating. The second class contains only a very small number of solutions; they are those of chromium sulphate, chloride, and nitrate, iodine, and perhaps potassium permanganate. These substances also possess one or two other properties in common. Thus they, all of them, crystallise without water of crystallisation. Solutions of none of them show regular changes in colour effect on dilution, and only chromium sulphate, and perhaps potassium permanganate solutions, decrease in colour at all. Coloured salts may thus be divided into two moderately well-defined classes. The salt potassium chromate presents a difficulty, however; for whilst, on the one hand, it does not crystallise with water of crystallisation, and does not decrease in colour on dilution, on the other hand it suffers very great increase of colour with rise of temperature.

The increments of colour of salt solutions on heating show general relations depending on the nature of the base of the salt, on the nature of the acid radicle, and on the degree of dilution of the solution. Thus, as a general rule, ferric salts are the most affected by temperature, then cobalt and uranium salts, then copper and nickel salts, and lastly potassium ferrocyanide and ferridcyanide. Again chlorides, with the exception of cobalt chloride, show the greatest increase; nitrates, with the exception of copper nitrate, come next, and sulphates last. With regard to the dependence of colour increase on dilution, all the sulphates show the greatest increase in their decinormal solutions, a lesser increment in their normal solutions, and the least in their centinormal. All chlorides, with the exception of ferric chloride, show the greatest increments in their normal solutions, a lesser increment in their decinormal solutions, and with the exception of cupric chloride the least increment in their centinormal solutions. The nitrates do not show such a general resemblance.

The colour effects of the solutions were determined at temperatures intermediate between 20° and 60°, in order to ascertain whether the colour effect increased at a rate proportionate to the temperature, or to some power of the temperature. Such relations could only be recognised with any certainty if they were well marked, and

occurred in a considerable number of salts; for all the numbers given are liable to an error of quite 2 per cent, or even more in some cases where the tint of the solutions changes on heating, and so renders comparison more difficult. Most of the numbers agree better on the supposition that the increase of colour is directly proportional to the increase of temperature, but in some, as the concentrated solutions of cobalt sulphate and nitrate, uranyl sulphate and acetate, ferric oxalate, and both solutions of acid ferric chloride, and also in some of the solutions of potassium chromate, bichromate, and chromium trioxide, the colour effect seems to increase at a greater rate than the temperature increases.

It has been shown that when solutions of nickel salts are heated they tend to turn yellow, the colour of their anhydrous salts; cobalt salt solutions tend to turn blue, the colour of their anhydrous salts. Blue solutions of cupric chloride tend to turn green, or to the colour of their more concentrated solutions; chromium trioxide solutions tend to turn more red, the colour of solutions containing free CrO_3 molecules; acid ferric chloride solutions tend to turn brownish yellow, the colour of their more concentrated solutions, and lastly, ferric oxalate solutions tend to turn from dirty green to brownish yellow, which is the colour of concentrated solutions of this salt. Thus in every case in which concentrated solutions of a salt have a different colour from the dilute solutions, it was found that on heating these dilute solutions their colour tends to change to the colour of their concentrated solutions. It is, therefore, a general principle which probably applies to all salt solutions, with one or two exceptions, as in the case of sodium sulphate and sodium carbonate, that the action of heat on a solution of a salt is to change the condition in which the molecules of the salt exist to the same condition they exist in in a more concentrated solution. Now all colorimetric determinations which bear on the subject at all prove that in the hot or in the concentrated solutions the molecules of salts tend to change their condition to that in which they exist in the anhydrous state; hence it is another general principle probably applying equally with the other to all salt solutions, that hot and concentrated salt solutions contain the molecules of salt combined with less molecules of water than cold or more dilute solutions. This is contrary to the conclusion of S. U. Pickering (*Chem. Soc. Journ.*, March, 1890), that the composition of hydrates in solution is not changed on variation of temperature.

Colorimetric determinations are thus without exception in favour of the hydrate theory of solution.

It may be said that as salts exist in dilute solutions in the same condition as in cold solutions, and as these show less colour effect than hot solutions, may not the decrease in colour effect of a salt on dilution be due to the same cause, viz., hydrates of less colour effect being formed. The observations detailed in this paper should in this case be taken to prove merely the existence of hydrates in solutions, and should afford no proof whatever of any dissociation taking place. This cannot be said to be the case, however. If it were so then the decreasing colour effects of solutions on dilution should be exactly proportional to the decreasing colour effects of the same salts on cooling their solutions, whereas it is nothing of the kind. Thus, to take a few instances, cupric nitrate solution decreases in colour effect on dilution more than cupric sulphate solution, but on heating the sulphate solution shows the greater increase. Cobalt chloride solution on dilution decreases in colour effect more than cobalt nitrate solution, but is more affected by rise of temperature.

Potassium chromate solution, though greatly affected by temperature, suffers no change at all on dilution. Chromium trioxide solutions, which are less affected by temperature than those of potassium bichromate, decrease in colour on dilution to nearly twice the extent. At the same time it cannot be denied that there is a general

resemblance between the two series of determinations. Thus of copper salts the acetate solution shows the greatest colour decrease on dilution and the greatest increase on heating. Cobalt salts show more dissociation than most other salts; they also show more colour increase on heating. Of uranium salts the chloride is most affected by dilution, and also by rise of temperature of its solution. Acid ferric chloride solution behaves similarly. Also it may be said that chromium salts, with the exception of chrome alum, show little if any increase in colour in their solutions on heating; that they therefore do not form hydrates in solution, and that this is borne out by the fact that they crystallise without molecules of water of crystallisation.

A great objection to this is that potassium chromate solutions—the great colour increase of which, on heating, must be due to the presence of hydrates—show no decrease of colour at all on dilution. Thus it would seem possible that the colour decrease of a solution on dilution need not necessarily be even in part due to the formation of fresh hydrates of less colour effect. It is probable, however, that in most cases it is due partly to dissociation and partly to the formation of hydrates of less colour effect. How much of the effect is due to each of these causes it is not possible to say, but it probably varies greatly with solutions of different salts.

On heating salt solutions the increase is probably wholly due to the influence of hydrates, for the dissociation values of solutions do not appear to vary with temperature. The increments of colour effect on heating for different salt solutions do not appear to bear any general relations to either the solubilities of the salts in water, or to the number of molecules of water of crystallisation they crystallise with.

(To be continued.)

A SIMPLE METHOD FOR DETERMINING THE WATER IN IODINE.

By Prof. Dr. MEINECKE.

For determining the water of crystallisation in iodiferous substances readily capable of decomposition, E. Ostermeyer passes the vapours of iodine and water, by means of a current of air, through a moderately heated combustion tube filled with spirals of sheet silver or copper, and allows the watery vapours, freed from iodine, to be absorbed in weighed drying tubes. When it is merely required to determine relatively small quantities of iodine, the metal spirals do good service; but as the proportion of moisture in iodine is generally small, it is desirable to take for its determination not too small a quantity of the material. Hence the danger that the iodine may escape absorption by the spirals is increased, except they are made of an inconvenient length.

My procedure, in which this risk is not merely obviated, but the apparatus is of the utmost simplicity, is as follows:—

The iodine to be examined is allowed to fall from the weighing-glass into a test-tube of about 1 c.m. in width and 6 c.m. in length; it is at once superstratified with from four to five times its quantity of silver powder, previously ignited; the tube is closed with a glass stopper, ground to fit its mouth, and weighed immediately; or, if in case of a high temperature of the air, the silver is being attacked by the iodine on mutual contact, not until completely cold. The open tube, which may be set in a small beaker, is heated upon an asbestos plate, so gently that only a very slow formation of silver iodide takes place. As this reaction can always be observed, it may be easily regulated in case of need by removing the beaker from the asbestos plate. With experience, which is easily acquired, there is no risk of the escape of even traces of iodine. Should it really occur, it would be inevitably shown by a

change of the colour of the silver powder; the silver powder then appears attacked to its upper layer, whilst if the operation is correctly managed, the upper portions of the silver must remain unchanged. During the formation of silver iodide, the water which escapes is condensed in the colder parts of the tube, from which, after the complete absorption of the iodine, it is expelled by a higher temperature. When this takes place, the tube is stoppered up, allowed to cool, and weighed. The difference shows the quantity of water which has been present in the iodine. The determination, with all the preparations, scarcely requires one hour.

The method allows of an accurate determination of moisture in iodine, even if chlorine and bromine are simultaneously present; it loses, however, its trustworthiness if considerable quantities of cyanogen are present.—*Chemiker Zeitung*.

HAMBURG WATER.

By JOHN B. COPPOCK, F.C.S.,
Analyst to the London Water Co.

THE spread of cholera at Hamburg has been one of the most noticeable points in the present cholera scare.

The connection between cholera and its diffusion in a polluted water medium has been strengthened and developed by many remarkable outbreaks extending over the last thirty years. The ravages of the disease have been shown to be coincident in time and space with the use of water from impure wells, the introduction of a pure and fresh supply bringing about the abatement of the outbreak.

Whether cholera can be produced by animal organic matters not of a specific nature has not yet been proved, but it has been proved that a polluted water supply is a splendid medium for the propagation of the cholera poison; anyhow, the endemic area of cholera approximates very closely to the area supplied with a polluted water.

By the kindness of a friend I have been enabled to get a sample of Hamburg Water taken from the mains by an ordinary tap, just as it is supplied for drinking purposes to the houses. The water gave the following results:—

PHYSICAL EXAMINATION.

Appearance	Turbid, very yellow.
Taste	Slightly unpleasant.
Odour	Extremely small.
Deposit	Small, dirty looking.

MICROSCOPIC EXAMINATION.

Animal and vegetable matters, inorganic particles.

QUANTITATIVE RESULTS (Mean of Two Analyses).

Total solids	81.25 grains per gal.
Chlorine	33.04 "
Free ammonia	0.0746 "
Albumenoid ammonia	0.0205 "
Sulphates	2.37 "
Nitrates	1.95 "
Oxygen (consumed in 15 mins.)	0.065 "
" (consumed in 4 hours)	0.24 "

Cultivation in nutrient gelatin produced the usual crop of bacteria, bacilli, micrococci and fungi, but the consumption of the water has not produced any choleraic symptoms in a cat. The water is very likely not specifically polluted, it producing a lowered state of the system and tendency to diarrhoea, favourable to the specific contagion. As the water is originally taken from the Elbe it may with fairness be described as little short of "dilute sewage." The Senate of Hamburg is going to be asked to authorise the immediate construction of

Artesian wells for the production of a pure water supply, —not too soon to take such steps in the present condition. A better water supply might have saved Hamburg from the present epidemic.

TENTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

THE Committee notes with satisfaction a growing appreciation of the Reports on Chemical Bibliography that have been presented to the Chemical Section of the American Association for the Advancement of Science. The Ninth Annual Report was widely circulated, appearing not only in the *Proceedings of the A. A. S.*, but also in the *CHEMICAL NEWS*, the *J. Anal. Appl. Chem.*, the *J. Am. Chem. Soc.*, and the *Scientific American*.

The Committee congratulates the Section on the fact that these annual reports have in large measure accomplished one of the principal objects sought, viz., that of directing attention to the importance of compiling bibliographies, catalogues, and indexes to the voluminous literature of chemistry. While little systematic work has been undertaken, duplication of labour has been prevented and independent efforts have accomplished much; how much appears in the list of bibliographies forming the Appendix to this Report. Chemists are more and more perceiving the advantages of attaching carefully prepared bibliographies to their monographs; recently this plan has been pursued in the important *Bulletins of the Chemical Division of the United States Department of Agriculture*. Thus a collection of special bibliographies is gradually forming, destined to be of inestimable value to the chemist. The Committee expresses the hope that this collection will grow in the future much faster than in the past, and suggests that members of the Section of Chemistry seriously consider in what way they can individually contribute to the cause.

During the current year the following indexes have been published.

1. A Bibliography of the Electrolytic Assay of Copper. By Stuart Croasdale. In *J. Anal. Appl. Chem.*, v., pp. 133 and 184 (March and April, 1891).
2. An Index to the Literature on the Estimation of Nitrogen by Kjeldahl's Method and its Modifications. By Lyman F. Kebler. In *J. Anal. Appl. Chem.*, v., 260, (May, 1891).
3. An Index to the Literature on the Estimation of Nitrogen by all other Methods. By Lyman F. Kebler. In *J. Anal. Appl. Chem.*, v., 264 (May, 1891).
4. Index to the Literature of the Tannins. By Professor Henry Trimble, Ph.M., of Philadelphia. This forms an Appendix to: "The Tannins; a Monograph on their History, Preparation, Properties, Methods of Estimation, and Uses of the Vegetable Astringents," by the author named. Philadelphia, 1892. Vol. I., 168 pp., 12mo. The Index occupies pp. 101—165, and the titles are arranged chronologically with an alphabetical index of authors. The whole is admirably printed and obviously exhaustive.
5. Index to the Literature of Angelic and Tiglic Acids, from 1842—91. By Henry P. Talbot, Ph.D. *Technological Quarterly*, vol. v., Nos. 1 and 2 (Massachusetts Institute of Technology, Boston). Contains an historical summary, and author- and subject-indexes.
6. Bibliography of Analytical and Applied Chemistry for the Year 1891. By H. Carrington Bolton. *J. Anal. Appl. Chem.*, vol. vi., p. 61, 1892.

We chronicle also the following contributions to chemical bibliography:—

7. Professor Thomas B. Stillman, in his papers on "Animal, Marine, and Vegetable Oils used in Lubrication," has paid especial attention to the bibliography of the subject, grouping under each division of his essay many references to periodical literature and other (*J. Anal. Appl. Chem.*, v., April, June, and December, 1891).

8. A list of Chemical Synonymes is found in pages 661—675 of the Appendix to "*The Scientific American Cyclopaedia of Receipts, Notes, and Queries*." Edited by Albert A. Hopkins. New York, 1892. 8vo. Ill.

9. Prof. Samuel P. Sadtler's "*Handbook of Industrial Organic Chemistry*" (Philadelphia, 1891, pp. xiv.—519. Roy. 8vo. Ill.) contains bibliographies at the close of each chapter embracing the following topics:—

- (1). Petroleum and Mineral Oil Industry.
- (2). Industry of the Fats and Fatty Oils.
- (3). Industry of the Essential Oils and Resins.
- (4). The Cane and Sugar Industry.
- (5). The Industries of Starch and its Alteration Products.
- (6). Fermentation Industries (Malting, Brewing Wines, Spirits, Vinegar, Flour, and Bread).
- (7). Milk Industries.
- (8). Vegetable Textile Fibres and their Industries.
- (9). Textile Fibres of Animal Origin.
- (10). Leather, Glue, and Gelatin.
- (11). Destructive Distillation Industries.
- (12). Artificial Colouring-matters.
- (13). Natural Dye Colours.
- (14). Bleaching, Dyeing, and Textile Printing.

The Bibliographies are chronologically arranged one-line titles.

Professor S. F. Peckham reports substantial progress on his Bibliography of Bitumen; Professor Arthur M. Comey on his Dictionary of Solubilities; and Dr. Alfred Tuckerman on his Bibliography of Mineral Waters. Dr. Arnold Eiloart, of New York, has completed the MS. of an Index to the Literature of Stereochemistry; this will appear as an appendix to his review of the subject in the *Am. Chem. J.* The whole will also be issued independently. Prof. Charles E. Munroe announces Part II. of his Index to the Literature of Explosives, to be published shortly. Dr. H. C. Bolton's Select Bibliography of Chemistry has been accepted by the Smithsonian Institution for its Miscellaneous Collections and is in the hands of printers.

H. CARRINGTON BOLTON, Chairman,
F. W. CLARKE,
ALBERT R. LEEDS,
ALEXIS A. JULIEN,
JOHN W. LANGLEY,
ALBERT B. PRESCOTT,
ALFRED TUCKERMAN.

APPENDIX TO TENTH ANNUAL REPORT OF COMMITTEE ON INDEXING CHEMICAL LITERATURE.

List of Indexes to Chemical Literature.

- Abbreviations of Titles of Chemical Journals.* By H. Carrington Bolton [and others]. *J. Anal. Chem.*, vol. ii., Part 1, Jan., 1888.
- Amalgams; Index to the Literature of.* By Wm. L. Dudley, in his Vice-Presidential Address to the American Association for the Advancement of Science, at Toronto. *Proceedings A. A. S.* for 1889, pp. 161—171, 1890. 8vo.
- Ammonia from Atmospheric Nitrogen, An Index of Researches upon the Production of.* By Ezra J. Ware. Published in *Proc. Michigan State Pharm. Assoc.*, 1888. H. J. Brown, Secretary, Ann Arbor, Mich.
- Analytical Chemistry, Bibliography of, for the year 1886.* By H. Carrington Bolton. *J. Anal. Chem.*, vol. i., pt. 3, July 1887.
- [The same] for 1887. *Idem.*, vol. ii., pt. 1, Jan., 1888.

* From Advance Proofs of the *Proceedings of the American Association for the Advancement of Science*, vol. xli., 1892.

- [The same] for 1888. *Idem.*, vol. iii., pt. 4, Oct., 1889.
- [The same] for 1889. *Idem.*, vol. iv., pt. 1, Jan., 1890.
- [The same] for 1890. *Idem.*, vol. v., No. 3, March, 1891.
- Analytical and Applied Chemistry**, Bibliography of, for the year 1891. By H. Carrington Bolton. *J. Anal. Appl. Chem.*, vol. vi., p. 61, 1892.
- Angelic and Tiglic Acids**, Index to the Literature of. By Henry P. Talbot. *Technological Quarterly*, Boston, vol. v., Nos. 1 and 2, 1892.
- Beeswax and Waxes Used in Adulterating Beeswax**, Bibliography of. By Harvey W. Wiley [Editor]. Foods and Food Adulterants. Part vi. *Bulletin* No. 13, Division of Chemistry, U.S. Department of Agriculture, Washington, 1892. 8vo., pp. 886—871.
- Butines and their Halogen Addition Products**, Index to the Literature of (1863—1888). By Arthur A. Noyes. *Technological Quarterly*, Boston, December, 1888. Published at the Massachusetts Institute Technology.
- Butter**, Bibliography of. By Elwyn Waller. In Second Annual Report of the N.Y. State Dairy Commissioner, 1886.
- Chemistry**, a Bibliography of, for the year 1883. By H. Carrington Bolton. In "An Account of the Progress of Chemistry in the Year 1883." Smithsonian Report for 1883. Washington, 1884. 8vo.
- [The same] for 1884, 1885, 1886, in Smithsonian Reports for said years.
- Chemistry**, a Bibliography of, for the year 1887. By H. Carrington Bolton. Washington, 1888. "Smithsonian Miscellaneous Collections," No. 665. 13 pp., 8vo.
- Columbium**, Index to the Literature of. 1801—1887. By Frank W. Traphagen. "Smithsonian Miscellaneous Collections," No. 663. Washington, 1888. pp. [iv.], 27, 8vo.
- Copper**, Electrolytic Assay, Bibliography of. By Stuart Croasdale. *J. Anal. Appl. Chem.*, v., 133 and 184. (1891).
- Electrolysis**, Index to the Literature of; 1784—1880. By W. Walter Webb. *Annals of New York Academy of Sciences*, vol. ii., No. 10, 1882. Pp. 44, 8vo.
- N.B.—This has been translated into French by Donato Tommasi, Paris, 1889.
- Explosives**, Index to the Literature of. Part I. By Charles E. Munroe. Baltimore, 1886. Pp. 42, 8vo.
- Part II. in press (1892).
- Food Adulteration and its Detection**, Bibliography of. By Jesse P. Battershall. In "Food Adulteration and its Detection." New York, 1887. 8vo.
- Geometrical Isomerism**, a Bibliography of. Accompanying an Address on this subject to the Chemical Section of the American Association for the Advancement of Science, at Indianapolis, August, 1890. By Robert B. Warder. *Proc. A. A. S.*, vol. xxxix., Salem, 1890, 8vo.
- Heat**, Dictionary of the Action of Heat upon certain Metallic Salts; including an Index to the principal literature upon the subject. Compiled and arranged by J. W. Baird; contributed by A. B. Prescott, New York, 1884, pp. 70, 8vo.
- History of Chemistry**, Outlines of a Bibliography of the. By H. Carrington Bolton. *Ann. Lyc. Nat. Hist.*, vol. x., pp. 352—361. New York, 1873.
- Honey**, Bibliography of. By Harvey W. Wiley [Editor]. "Food and Food Adulterants," Part vi. *Bulletin* No. 13, Division of Chemistry, U.S. Department of Agriculture, Washington, 1892, 8vo., pp. 871—874.
- Iridium**, Bibliography of the Metal. By Nelson W. Perry, in Prof. W. L. Dudley's paper on Iridium, published in "Mineral Resources of the United States," calendar years 1883 and 1884. Washington, 1885, 8vo.
- Light**, Chemical Influence of, a Bibliography of. Alfred Tuckerman. "Smithsonian Miscellaneous Collections," No. 785, Washington, 1891, pp. 22, 8vo.
- Manganese**, Index to the Literature of; 1596—1874. By H. Carrington Bolton. *Annals of the Lyeum of Natural History*, New York, vol. xi., November, 1875, pp. 44, 8vo.
- Milk**, Bibliography of. By Edward W. Martin. In Second Annual Report of the N. Y. State Dairy Commissioner. 1886.
- Nitrogen**, Estimation of. By Kjeldahl's Method, Index to the Literature. By Lyman F. Kebler. *J. Anal. Appl. Chem.*, v., 260 (1891).
- Nitrogen**, Fixation of Atmospheric. For bibliographical data see Historical Summary on this subject by A. A. Breneman in *J. Am. Chem. Soc.*, xi. (1889).
- Ozone**, Index to the Literature of; 1875—1879. By Albert R. Leeds. "Annals of the New York Academy of Sciences," vol. i., No. 12, 1880, pp. 32, 8vo.
- Ozone**, Index to the Literature of, 1879—1883; accompanied by an Historical Critical Résumé of the Progress of Discovery since 1879. By Albert R. Leeds. *Annals N. Y. Academy of Sciences*, vol. iii., p. 137, 1884. 16 pp., 8vo.
- Periodicals**, A Catalogue of Chemical. By H. Carrington Bolton. *Annals N. Y. Acad. Sci.*, vol. iii., pp. 159—216. New York, 1885. 8vo. Also: CHEMICAL NEWS Print, London, 1886. 12mo.
- Supplement to (the same). *Ann. N. Y. Acad. Sci.*, vol. iv., Feb., 1887. 4 pp., 8vo.
- Periodicals**, Short Titles of, current in 1887. By H. Carrington Bolton. *J. Anal. Chem.*, vol. i., Part 1, 1887. 4 pp., 8vo.
- Peroxide of Hydrogen**, Index to the Literature of; 1818 to 1878. By Albert R. Leeds. *Annals N. Y. Acad. Sci.*, vol. i., No. 13, 1880. 11 pp., 8vo.
- Peroxide of Hydrogen**, Index to the Literature of; 1879 to 1883. By Albert R. Leeds. *Annals N. Y. Acad. Sci.*, vol. iii., p. 153, 1884. 3 pp., 8vo.
- Petroleum**, A Bibliography of. By Prof. S. F. Peckham. Report on the Production, Technology, and Uses of Petroleum and its Products. Report of the Census of the United States. Vol. x., 1884. 4to, pp. 281—301.
- Ptomaines**, A Bibliography of; accompanies Victor C. Vaughan's Ptomaines and Leucomaines, Philadelphia, 1888, pp. 296—314, 8vo.
- Speed of Chemical Reactions**, Literature of. By Robert B. Warder. *Proc. Amer. Assoc. Adv. Sci.*, vol. xxxii., 1883. 3 pp., 8vo.
- Specific Gravity of Solids and Liquids**, A Table of. The Constants of Nature, Part 1 (new edition, revised and enlarged). By Frank Wigglesworth Clarke. Washington, 1888. Smithsonian Miscellaneous Collections, No. 659, pp. 11—409, 8vo.
- Spectroscope**, Index to the Literature of. By Alfred Tuckerman. Smithsonian Miscellaneous Collections, No. 658. Washington, 1888, pp. 10—423, 8vo.
- Starch Sugar**, Bibliography of. By Edw. J. Hallock. Appendix E to Report on Glucose prepared

- by the National Academy of Sciences, in response to a request made by the Commissioner of Internal Revenue. U. S. Internal Revenue, Washington, D. C., 8884. 44 pp. 8vo.
- Tannins**, Index to the Literature of. By Henry Trimble. The Tannins. Philadelphia, 1892. Vol. i., Appendix.
- Tea, Coffee, and Cocoa Preparations**, Bibliography of the Literature on. By Guilford L. Spencer. Food and Food Adulterants. Part vii., Appendix A. *Bulletin* No. 13, Division of Chemistry, U. S. Department of Agriculture. Washington, 1892. 8vo., pp. 991—1009.
- Thermodynamics**, Index to the Literature of. By Alfred Tuckerman. Smithsonian Miscellaneous Collections, No. 741. Washington, 1890. pp. 6—329. 8vo.
- Titanium**, Index to the Literature of; 1783—1876. By Edw. J. Hallock. *Annals of the New York Academy of Sciences*. Vol. 1, Nos. 2 and 3, 1877. 22 pp., 8vo.
- Uranium**, Index to the Literature of. By H. Carrington Bolton. *Annals of the New York Lyceum of Natural History*, Vol. ix., February, 1870. 15 pp. 8vo.
- Uranium**, an Index to the Literature of; 1789—1885. By H. Carrington Bolton. Smithsonian Report for 1885. Washington, 1885. 36 pp., 8vo.
- Vanadium**, Index to the Literature of. By G. Jewett Rockwell. *Annals of the New York Academy of Sciences*, Vol. i., No. 5, 1877. 32 pp., 8vo.

A PROCESS FOR THE REMOVAL OF THE LINT FROM COTTON-SEED.*

By WM. L. DUDLEY.

THE "sea-island" or "long-staple" cotton (*Gossypium Barbadosense*) and the Egyptian cotton have naked seed, while the "upland" or "short-staple" cotton (*G. Herbaceum*) of the United States has seed encased in a mass of fibre firmly adherent to the seed-coat.

The seed crushed in England for the extraction of the oil is largely the Egyptian, but in the United States the great source of the oil is the "upland" seed, as the "sea-island" cotton grows over a very limited area. In consequence of this hairy envelope which surrounds the American cotton-seed, decortication is necessary previous to the expression of the oil. The Egyptian and "sea-island" seed need only be crushed, heated, and pressed.

Besides the expense of decorticating the American seed, much "meat" is lost by becoming entangled in the hulls and failing to separate; on this account the oil-yield is lower by several gallons per ton than that from the naked seed, and the yield of "cake" is less as it contains no hulls. The American seed will not stand storage nor shipment well (especially export), as moisture absorbed by the fibrous envelope will enable fermentation to set in.

The process for the treatment of American seed is briefly as follows:—They are (1) run through "linters," which remove as much as possible the cotton which has been left on the seed by the gin; (2) decorticated by a machine which cuts the seed-coat, whereupon the "meat" and the "hulls" fall apart; (3) separated by passing through an inclined revolving screen having meshes which allow the "meat" to fall through, while the "hulls" are retained and roll out at the lower end; or by means of an air blast; (4) the "meat" is heated and

pressed. The hulls are burned, and the ash, rich in potash, has a market value.

All mechanical methods which have been devised to strip the seed of its fibre have proved unsuccessful, either from imperfect performance or lack of speed.

The chemical process described below was devised some time since (U.S. Pat. 344,951) by the author and N. W. Perry, E.M. It has never been tried commercially, but its success is perfect on a small scale.

The seed after linting are subjected to the action of N_2O_3 and SO_2 , either in the above order or mixed together, enough air attending them to "regenerate" the NO . This is probably best accomplished by having the seed descend a chute slowly through which a current of N_2O_3 is ascending, and then into a chute where SO_2 and air are ascending; or they may descend through a chute having an ascending current of N_2O_3 , SO_2 , and air. After a few seconds' exposure to these gases under proper conditions, the fibre on the seed has changed very little in appearance, but its structure is so completely destroyed that the slightest friction causes it to fall into an impalpable powder. The seed are left perfectly smooth, showing no signs of corrosion. They have a slight acid reaction on the outside, but the acid is speedily removed by washing. The seed-coat is very hard, and is impervious to the gases. No trace of acid has ever been discovered in the interior. The seed germinate very quickly if planted. The acidity may also be removed by blowing lime-dust on the seed as soon as they come from the "cleaner" which removes the disintegrated fibre; or they may be carried by a conveyer through lime-water and then through a dryer. The seed are now ready to be crushed and pressed, or they may be shipped and stored as well as Egyptian or "sea-island" seed.

The "cleaner" referred to above may be any good grain cleaner. The disintegrated fibre is quite dry, and is easily converted into glucose.

The N_2O_3 and SO_2 may be generated by any of the well-known processes, but the ordinary methods employed in sulphuric acid making are the most economical. In fact this process should be operated, possibly, in connection with such works; the gases escaping from the cotton-seed chute being absorbed in the tower or conveyed into the leaden chamber, so that there is no loss.

NOTICES OF BOOKS.

Photography Annual. A Compendium of Information upon Photographic Matters and the Annals of Photography for the Past Year, 1892. By HENRY STURNEY. London: Iliffe and Son, 3, St. Bride Street, Ludgate Circus, E.C.

THIS goodly volume opens with a collection of tables, &c., useful to the photographer, though not to him alone.

We notice a table of poisons with characteristic symptoms and antidotes. We presume the author has purposely mentioned those only which the photographer is liable to encounter in his *atelier*. We may here repeat a caution which we have given elsewhere, that no food or drink should be partaken of in laboratories, dye, print, or colour works, or in other localities where chemical operations are carried on.

The list of impurities liable to be present in chemicals will be very useful, especially to the beginner who has not got into the habit of suspecting possible impurities everywhere until he has proved their absence.

We cannot help applauding the remark that "an east wind means bad light, however otherwise bright the day may seem to appear."

The advances made in various sciences by means of photography are chiefly in the direction of astronomy. Chemistry and biology seem to be reaping little direct advantage. Nevertheless, the photo-micro apparatus

* *Journal of Analytical and Applied Chemistry*, Vol. vi., No. 3.

here shown and described (Nos. 109 and 110) will be of great value to the student and the "researcher,"—if we may venture upon this ugly word.

Considering the thoroughly technical character of most of the subject-matter, the typographical accuracy of the work deserves commendation. We notice one error, where "Coleoptera" is transformed into "Coloptera."

The list of the photographic societies of the United Kingdom is wonderful in its extent. Here we are led to a question; we believe and hope that the scientific applications of photography are as yet only in their infancy, and that developments are here in store which are yet quite unexpected. But will the rage for photography as a mere amusement prove permanent? In all human probability not. The professional photographers, the art students, and the men of science to whom the camera with its accessories rank with the microscope, the spectro-scope, and the balance will scarcely suffice to keep in action the legion of makers and sellers of apparatus and the really respectable number of journals devoted to the subject.

A Pocket-Book for Miners and Metallurgists. Comprising Rules, Formulæ, Tables, and Notes, for use in Field and Office Work. Compiled by FREDERICK DANVERS POWER, F.G.S. London: Crosby Lockwood and Son, 1892. 12mo, pp. 334.

THIS is one of those thoroughly practical works with which Messrs. Crosby Lockwood and Son are enriching our technological literature. Almost the only error which we can detect is in the table of atomic weights; platinum is given = 196.7, i.e., higher than gold, whilst according to the latest and most accurate determinations it is only 195.

We regret to find Baumé's table for the specific gravities of liquids inserted. It has the twofold defects of being not reducible to direct specific gravity by any simple calculation, and of existing in three discordant modifications. For what purpose it is retained in France and America we are unable to say. A few typographical errors in a work of such technical character can scarcely be avoided. In the section on toxicology we find "dantrin" for "daturine."

The table for calculating the results of chemical analyses strikes us as being much less convenient than that of Rose. The index is very good and the glossary will prove widely useful, since in these days a specialist is often puzzled if he encounters some term belonging to a different speciality. We trust this work will be as widely appreciated as most of its predecessors have been.

The Extra Pharmacopœia. By W. MARTINDALE, F.C.S. Medical References and a Therapeutic Index of Diseases and Symptoms. By W. WYNN WESTCOTT, M.B. Seventh Edition. London: H. K. Lewis, 1892.

MEDICAL science knows no finality. If there are certain diseases which still set the physician at defiance it must be admitted that, as shown by the little volume before us, the latter is constantly adding to and modifying his armoury.

Turning over the leaves we find mention of the double gold and sodium chloride used as an antidote to cobra-poison. But with what success? It must cheer the heart of Bishop Berkeley, if he still studies medical literature, to find that tar and its preparations are again coming more to the front.

A Russian remedy for dropsy which must appal the fair sex consists simply of powdered cockroaches, the "black beetles" of kitchen entomology. As there are a few of these insects in London, it might be well if some enterprising quack would bring them into vogue as a medicine. In sober sadness it is folly to assume that we have yet exhausted nature's resources for the relief and the prevention of disease. Our duty plainly is to go on trying

"all sorts of things" with due scientific precaution until the black list of "opprobria medicinæ" is effaced. The busy practitioner will find the work of Messrs. Martindale and W. W. Westcott exceedingly suggestive.

Catalogue of Standard Second-Hand and New Books, English and Foreign, on Chemistry and the Allied Sciences. Offered by WILLIAM F. CLAY. Edinburgh: University Book Warehouse, 18, Teviot Place.

THIS issue of Mr. W. F. Clay's catalogue presents as a most striking feature complete sets of standard journals, transactions, &c., scarce and often very difficult to obtain, yet offered at exceptionally moderate prices. We may mention as instances a complete set of the reports of the British Association from the commencement in 1845 to 1888; the CHEMICAL NEWS from its commencement in 1860 to the end of last year; the *Journal of the Chemical Society* in fifty-eight volumes, from 1848 to 1890; the *Journal of the Society of Chemical Industry* complete, from the beginning; the *Philosophical Magazine* in 196 volumes, from 1798 to 1890, besides a multitude of rare and valuable chemical and physical works.

The librarians of universities, &c., as well as private collectors of works in any particular department of Science, will find this catalogue an excellent guide to the completion of their sets and the acquisition of desiderata.

The Principal Starches Used as Food. Illustrated by Photo-micrography, with a short Description of their Origin and Character. By W. GRIFFITHS. 62 pp., 25 Photomicrographs. Cirencester: Bailey and Son.

THE object of the author in the publication of this little work is to aid analysts in the identification of such starches as may be met with in the course of their investigations. Starch is so much in use for purposes of substitution or adulteration, that any means by which its fraudulent use can be detected must prove of the greatest utility.

The microphotographs are carefully executed from verified specimens, in most instances prepared by the author himself. They are all photographed under the same magnifying power ($\times 160$), which will aid comparison with other specimens. A short description is given of each starch represented.

One of the most interesting starches, both from its large size and the distinctness of its structural details, is that from the fruit of the potato (*Solanum tuberosum*),—a Jupiter among starches. It is somewhat remarkable that no trace of starch has up to the present time been discovered in the fruit of a closely allied plant, the tomato. This starch, as the author remarks, would be the most suitable on which to carry out investigations relating to its physical structure. The nature of the beautiful concentric markings is still unknown. The chemistry of starch being so fully treated elsewhere is but little mentioned in the present book, and as it is not possible by chemical means to discriminate between the starch of one plant and that of another, the omission is of little moment.

For these determinations the microscope is the only reliable guide; and to the analyst whose work leads him to researches on the admixture of cheaper starches with the more costly, as well as to their use in adulterating other substances, the book and its illustrations must prove of the greatest value.

Everybody's Pocket Cyclopædia of Things worth Knowing. By DON LEMON. London: Saxon and Co.

THE success of the previous editions of this useful reference book has justified the compiler in making many additions to this, the tenth. The pocket-book is almost double the size that it was when first published four years ago, and during that time about 500,000 copies have been

sold. There are, however, still a few alterations which might with advantage be made; for instance, the tables on pages 58, 96, and 97 cannot be properly read without turning the book upside down, but this could easily be rectified. Further, the bulk of page 84 might be omitted, it being merely an old arithmetical puzzle of "how to tell a young lady's age."

These are but minor defects in the book, and do not detract from its value in many other points. It is furnished with an excellent index and is very clearly printed.

The Threshold of Science. By Dr. C. R. ALDER WRIGHT. Second Edition. London: Charles Griffin and Co.

THE number of elementary works of this class published of late years shows that the demand for them is always increasing. Being written with the object of providing a kind of "playbook," which will amuse and at the same time instruct, the "Threshold of Science" is well adapted as a book for boys, giving, as it does, a good insight into the various branches of chemical and physical science, and stimulating a desire for further knowledge. System is becoming so intimately associated with modern everyday life and work that our children cannot too early be given that thirst for knowledge which will so materially assist them in later years.

Constable's Oriental Miscellany. Vol. II. *Popular Readings in Science.* By JOHN GALL, M.A., LL.B., and DAVID ROBERTSON, M.A., LL.B., B.Sc. London: Archibald Constable and Co.

THE authors of this work are certainly to be congratulated upon the very great amount of interesting matter comprised within its limits; we may say that there is scarcely a dull page in the whole volume. It consists, as its title would indicate, of various articles treating of and discussing different modern theories in chemical and allied branches of science; a large part of the book deals with evolution, not only in living bodies and plants, but even going so far back as to apply modern theories to the formation of matter itself, and its subsequent "contraction"—if we may use the term—into elements, suns, planets, &c.

One cannot help being struck by the manner in which these theories seem to spring from Darwinism, as well as the way in which they fit in one with another. The authors lay no claim to originality, but have embodied in their articles the best accepted theories and speculations of recent times. A feature of this book which must not be overlooked is the supply of about half a dozen catalogue slips; there is, however, in this, room for improvement, as these slips, being all the same, give prominence to the name of one of the authors only, while there is no slip whatever with the name of the book itself coming first.

CORRESPONDENCE.

STILLS AND THE EXCISE.

To the Editor of the Chemical News.

SIR,—It may be of interest to your readers to know that the following letter has been received from the Excise Authorities in reply to a memorandum laid before them by Mr. Carteighe (Vice-President), in accordance with the request of the Council of the Institute of Chemistry.—I am, &c.,

G. H. ROBERTSON, Secretary.

The Institute of Chemistry,
9, Adelphi Terrace, Strand, W.C.
Sept. 10, 1892.

Inland Revenue, Somerset House,
London, W.C.

SIR,—Having laid before the Board of Inland Revenue your letter of 28th July, I am directed in reply to acquaint you, for the information of the Council of the Institute of Chemistry, that the Board have no desire to extend the obligation to take out a licence to analytical chemists using stills solely for purposes of distilling water. If an analytical chemist called upon to take out a licence by one of the Board's officers will submit his case to the Board they will be prepared to give the matter careful consideration.—I am, Sir, your obedient Servant,

(Signed) W. B. HERBERTEN,
To M. Carteighe, Esq. Asst. Secretary.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 6, August 8, 1892.

Application of the Measurement of Densities to the Determination of the Atomic Weight of Oxygen.—A. Leduc.—The author gives the molecular weight of the vapour of water as 17.88. Its theoretical density, taking that of hydrogen as a point of departure, would be 0.6212. But it is preferable to set out from the density of oxygen, the compressibility of which is scarcely superior to that of air. We thus arrive at 0.6221. We see that the experimental density of the vapour of water cannot descend below 0.622.

The General Form of the Curves of Ebullition of Compounds with Central Substitution.—G. Hinrichs.—A very mathematical paper, which requires the reproduction of the very complicated diagram.

Existence in Soils of an Acid Mineral Substance not yet Determined.—Paul de Mondesir.—The substance which the author points out is very stable. It is not destroyed on the complete combustion of the organic matter at dull redness, even when deprived of its bases by previously washing the soil with dilute acids. It resists to a great extent hot, concentrated hydrochloric acid, which dissolves all the iron that gives a red colour to burnt soils and likewise nitric acid boiling for some hours. It is preserved almost entirely in soil submitted to ebullition for two or three minutes in a solution of caustic potassa containing about 15 per cent of actual potassa. The author has not yet been able to determine its composition. It is probably a silicate of a clayey character.

Calcareous Soap and the Explosions of Steam-Boilers.—A. Vivien.—The author does not consider the formation of this lime-soap proved. The crock formed in the boilers is not found to contain fats or fatty bodies, and the alleged lime-soaps contained only from 0.160 to 0.000 of fatty matter.

On Pupine, a New Animal Substance.—Dr. A. B. Griffiths.—Pupine is extracted from the integuments of lepidopterous pupæ. Its mean composition is $C_{14}H_{20}N_4O_5$. It is colourless and amorphous. It dissolves in mineral acids, being converted into leucine and carbonic acid. It is not dissolved by neutral solvents.

Colouring-Matter of Micrococcus Prodigiosus.—Dr. A. B. Griffiths.—The mean composition of this pigment is $C_{38}H_{56}NO_5$. The alcoholic solution shows with the spectroscope two absorption-bands, one in the blue and the other in the green. Acids turn it to a carmine and alkalis render it yellowish. This parasite

may be completely destroyed by syringing the crops with a solution of ferrous sulphate.

Vol. cxv., No. 7, August 16, 1892.

Certain New Compounds of Piperidine.—Raoul Pictet. — Piperidine, a secondary base, yields with salts of silver compounds much more stable than those resulting from the union of pyridine, a tertiary base, with the same salts. In pyridine the facility of combination with salts of silver increases from the chloride to the bromide and the iodide. In piperidine the inverse order prevails. Silver chloride fixes 2 mols. $C_5H_{11}N$; the combination of this salt with C_5H_5N is not stable at the ordinary temperature. Silver bromide and cyanide fix 2 mols. $C_5H_{11}N$ and only 1 mol. C_5H_5N . Silver iodide fixes only 1 mol. of each of these bases.

Application of Chemical Analysis to Fix the Age of Præhistoric Human Bones.—Ad. Carnot. — The author draws conclusions from the comparative proportion of fluorine, which is found to be larger the older the bones.

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Zeitschrift für Analytische Chemie.
Vol. xxx., Part 6.

(This issue has appeared only after the two first parts of Vol. xxxi.).

Determination of Oil of Mustard.—Dr. A. Schlicht. — This paper will be inserted at length.

The Question of the Fermentability of Dextrines.—L. Medicus and C. Immerheiser. — The authors decide that the dextrines of crude potato-sugar are capable of fermentation if a sufficient quantity of "press yeast" is applied, though it resists beer yeast.

Different Solubilities of Strontium and Calcium Chromates in dilute Alcohol, and on the Possibility of Separating these Two Alkaline Earths as Chromates.—W. Fresenius and F. Ruppert. — A useful qualitative separation can be founded upon the differences recognised if the quantities of strontium are not too small, but it does not suffice for a quantitative separation.

Determination of the Specific Gravity of Sparingly Fluid Substances.—J. W. Bruehl. — Already inserted.

Apparatus for Determining Refractive Power.—J. Bernström (German patent). — This apparatus is identical with Söndén's liquoscope.

Air Thermometer for Technical Purposes.—A. H. Sabine. — (From the *Journal of the American Chemical Society*).

Apparatus for Determining the Temperature of Explosions.—S. Bein. — Already inserted.

Agitation Apparatus for Electrolytic Operations.—N. von Klobulow. — (From the *Journal für Praktische Chemie*).

Development of Gases.—E. Dossaert (*Chem. Zeit.*). — A sulphuretted hydrogen apparatus. Similar in principle is the gas generator of W. Oakes Kibble described and figured in the *CHEMICAL NEWS*. A gas apparatus which may be extemporised in any laboratory is that proposed by Eustace Thomson in the *CHEMICAL NEWS*. Other apparatus for generating gases have been proposed by Grünwald (*Chemiker Zeitung*), Raikow (*ibidem*), and Habermann (*Naturf. Verein in Brunn*).

Hydrogen Sulphide free from Arsenic.—M. Habermann. — Already inserted.

Preparation of Pure Hydrogen.—M. Berthelot. — (From the *Bull. Soc. Chim. Paris*).

Development of Gases.—W. H. Hillyer (*Amer. Chem. Jour.*) and Pollak and Wilde (*Chemiker Zeitung*) have drawn attention to the proposal of letting the acids fall drop by drop upon a sufficiently deep stratum of the solid ingredient, so that the acid is thoroughly utilised before it flows away.

Production of Oxygen.—J. Volhard (*Liebig's Ann.*), employs the mutual reaction of hydrogen and chloride of lime.

Production of Oxygen.—G. Kassner (*Chem. Zeitung*), employs the reaction of potassium ferricyanide with hydrogen peroxide in presence of alkali.

Development of Gases.—M. Neumann (*Ann. für Prakt. Chemie*). — Already inserted.

Hydriodic Acid.—E. Etard (*Bull. Soc. Chim. Paris*), obtains a continuous current without disconnecting the apparatus by means of a flask with a lateral tubulure, through which passes the gas delivery tube.

Some New Small Laboratory Appliances.—S. Schiff (*Chemiker Zeitung*), and Fr. Stolba (*Berichte der böhm. Gesell. der Wissenschaft*). — Both devices are figured and described here.

A Closure for Burettes without a Cock.—M. Dannbacher (*Pharm. Central Halle*). — Already inserted.

New Stopper for Reagent-Bottles.—A. Gawalowski. — Already inserted.

Ground Joints and Glass Cocks for Vacuum Apparatus.—W. A. Shenstone. — (From the *Journal of the Chemical Society*).

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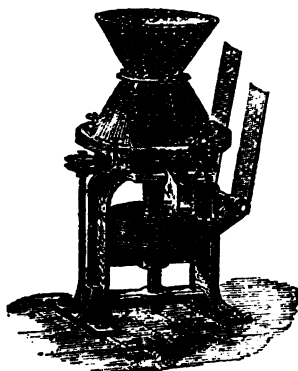
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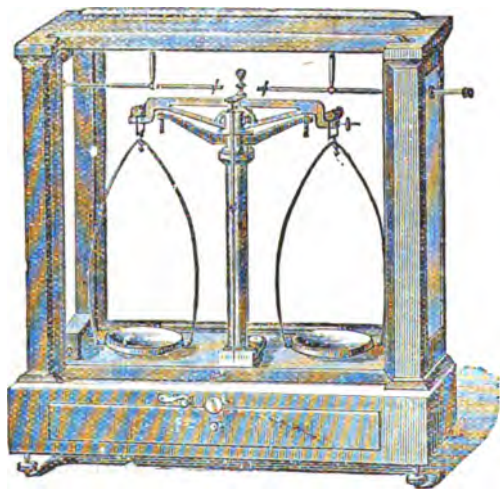


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ON THE COMPOSITION OF SEA-WATER.

By DR. F. GIBSON.

It is not possible to obtain a really accurate direct determination of the total salts contained in sea-water, as, during the course of evaporation, however carefully conducted, indeterminate quantities of carbonic acid from the bicarbonates are given off, owing to the fact that magnesium chloride decomposes. For the purposes of comparison and hydrographical record, the relative proportion of total salts in different sea-waters is most generally, and also most accurately, derived from a determination of the density of the sea-waters in question. Dittmar came to the conclusion, from an elaborate examination of sea-water collected during the *Challenger* expedition, that different samples of sea-water differed from one another, in so far as any rate as the saline constituents were concerned, simply by the amount of water which they contained,—that is to say, they might be more or less diluted, but the relative proportions of the saline constituents to one another was constant. If this could be laid down as a practically general rule it is obvious that, instead of a determination of density, one might rely equally upon the determination of one of the principal saline constituents. It would be simply a question as to which method was at once the most accurate and most easy.

This is not, however, an altogether easy matter to decide, and authorities differ, some considering determinations of the chlorine more accurate and others a determination of the density. The fact is that, if a high degree of accuracy is necessary, both are difficult. For the purposes of a mere comparison of salinities, it appears to me that there can be little doubt that preference should be given to density determinations by means of hydrometers such as have been used so successfully by Mr. J. Y. Buchanan. It is, however, very obvious that the relative proportions of the salts in sea-water must be altered more or less, when sea-water is mixed with water draining from the land. The amount of alteration will depend not merely upon the quantity of land-water mixed with the sea-water, but also upon the nature of the land-water itself. Thus the water pouring into the Moray Firth from the Rivers Spey and Findhorn makes a scarcely appreciable difference in the relative proportions of the saline constituents, because these waters are exceptionally pure. On the other hand, the river-water flowing into the Baltic has a very appreciable effect upon the chemical composition of the saline constituents, so that by determining accurately the composition of a Baltic water and Moray Firth water, of the same density, we should find a very appreciable difference between the two. We should find, for instance, the percentage of chlorine lowered as the percentage of sulphuric acid increased in the Baltic water. A still more marked difference will be found in the proportion of carbonates, which would be much greater in the Baltic water. It will be observed that this question of the difference of composition of the saline constituents must be clearly distinguished from any question of mere alteration in density or salinity, and would remain altogether undetected if either of the two methods referred to above were applied singly to such waters. Any mere determination of the density or of the chlorine, considered separately, would throw no light whatsoever upon this question; but if sufficiently accurate determinations of both the percentage of chlorine and density were taken, the difference would become at once manifest.

Dittmar, in formulating his proposition that the relative proportion of the saline constituents of true ocean-water is practically constant, made use of the following formula:—

$$\frac{S - W}{4t4t} = D$$

X

In this formula X is the weight of chlorine in a thousand parts of the sea-water, or, more correctly, the total halogen (chlorine, bromine, and iodine) calculated as chlorine.

S, signifies specific gravity of sea-water; W, specific gravity of distilled water; the subscript numeral to the left of the letters indicates the temperature at which a volume of distilled water is considered to represent unit weight; the subscript *t* to the right of the letters indicates the temperature at which the respective specific gravities are taken.

The value of the above ratio is, according to Dittmar, constant. As the salts derived from the drainage of land contain relatively large proportions of carbonates and sulphates along with a relatively very small proportion of chlorides, it is obvious that the value of the above ratio must be altered when sea-water is mixed with land-water. Dittmar determined the value for this ratio, and found it equal to 1.4600. In 1883 this ratio was determined for a number of samples collected from different parts of the Moray Firth, and of widely varying density. Some were collected far out to sea; others were collected near the mouths of rivers and far up the Inverness Firth; these samples of course having very low density or salinity. The value for the above ratio, however, in all the different samples approximated closely to the value found by Dittmar. The meaning of this is simply that the ratio of the saline constituents to one another had not been altered, and the explanation of this somewhat unexpected result is to be found in the great purity of the land-water flowing into the Moray Firth. Certain samples collected in the Baltic in 1886 gave very different results. In these samples the salinity or density decreased, of course, as the distance from the sea increased; that is to say, the further from the sea and the further into the Baltic, the lower the density of the water, which should be mixed with a large proportion of the land-water flowing into the Baltic. The value of the above ratio, or, for the sake of brevity, the value for "D," increased as the density or salinity increased.

Now this change in the value for "D" indicates simply a change in the ratio of the salts of the saline constituents to one another, according to the proportion in which the sea-water was diluted by the land-water of different saline composition flowing into the Baltic. The percentage of chlorine diminished because the percentage of chlorine in the saline constituents of the river-waters is very much smaller than in the saline constituents of sea-water proper. Thus an increase in the value for "D" results from admixture of sea-water with the land-water, whenever the land-water contains an appreciable quantity of salts, as the saline constituents of land-water contain invariably a small proportion of chlorine; but such brackish water will also be characterised in a second manner, and to this I wish to call special attention, because, as will be seen later on, an alteration in the value of "D" does not necessarily indicate admixture of sea-water with land-water.

The saline constituents of river-water contain a relatively large proportion of carbonates; that is to say, constituents capable of neutralising hydrochloric acid. If we take "A" as representing the weight in grammes of carbonic acid equivalent to the hydrochloric acid required to neutralise 1000 parts of sea-water, or what is usually known as the alkalinity, and substitute "A" for "X" in the above ratio, we should, in the case of ocean-water proper, on Dittmar's supposition, have constant

value from this ratio also, which we may call "D A"; but in the cases of such samples of brackish water as were collected in the Baltic it will invariably be found that the value for "D A" decreases as the value for "D" increases; that is to say, the alkalinity, or, in other words, the proportion of carbonates in such waters, increases as the proportion of chlorine decreases, so that ocean-water when mixed with land-water will show an increased value over "D," signifying a lower percentage of chlorine in the total salts, and an increased value for "D A" signifying an increase in the proportion of carbonates in the total salts.

It will be remembered that the samples collected in the Moray Firth in 1883, although of greatly varying density, many of them being largely mixed with land-water, all gave a ratio for "D" approximating closely to Dittmar's value for ocean-water. In 1886 a second batch of samples was collected from the Moray Firth. As before, they varied greatly in density, according to the position in which they were taken; that is, according as they were more or less diluted with river-water. The value of "D" was found nearly constant in all these samples, but was altogether different from that obtained previously. Remembering the great purity of the waters flowing into the Moray Firth, the difference in the chemical composition of the saline constituents implied by this new value for "D" seemed almost unaccountable, and it was natural to suspect some flaw in the methods of observation. Fortunately the density and the chlorine of some samples of water collected in 1883 had been determined. As these determinations were made with the same instruments, the same standard solutions, and at the same time as the determinations of the second batch of samples, and as the determinations were moreover all completed before any of the results were calculated, it was obvious that, if this change in the value of "D" were in any sense due to the method of working, this would have its effect upon the results obtained with these samples. Now these samples collected in 1883 all gave practically the same value for "D" as they had done before when first analysed. This in fact constituted a cross test of the most stringent character. There was therefore no escape from the conclusion that the two different values for "D" corresponded to two distinct kinds of sea-water, because, as will be observed, the increase in the value of "D" cannot be accounted for by admixture with the extremely pure waters flowing into the Moray Firth.

During subsequent cruises of H.M.S. *Fackal*, in the North Sea, evidence was in point of fact obtained that there are two kinds of sea-water in the North Sea.

Had we nothing to guide us but determinations of the value of "D" it might, by a great stretch of imagination, be supposed that these remarkable differences in the value for "D" were due to admixture of ocean-water proper with such water as flows into the Baltic, though it would be necessary to suppose that these waters had become concentrated by evaporation to about one fourth of their original bulk, because it was not until the salinity of the samples collected in the Baltic had decreased to about one-fourth of the salinity of normal sea-water, such as is found in the middle of the North Sea, that the value for "D" had increased so much as to become equal to the value for "D" in this second batch of Moray Firth samples. But this idea is entirely negated by the fact that, although the value for "D" was greatly increased in these samples, the value for "D A" remained practically constant. It is impossible to reconcile this with the supposition that the alteration in the value of "D" is simply due to admixture with land-water. To sum up:—

The value for "D" in thirteen 1883 samples varied within the limits of 1.4595 and 1.4551. The value for "D" in the forty-five samples collected in 1886 varied within the narrow limits of 1.4675 and 1.4735, and only four samples gave a value lower than 1.4700.

Off the north coast of Scotland, in Jan., 1889, twelve samples varied within 1.4576 and 1.4555.

Seven samples from high northern latitudes (between 62° and 79° N. lat.), in summer, 1888, varied from 1.4726 to 1.4704.

The only cause which seems to the author sufficient to account for these differences is admixture with water derived from the melting of Arctic water ice. According to Pettersson's observations the water obtained by melting sea-water ice from Arctic regions, and also from the Baltic, contains a much higher proportion of sulphates to chlorides than that characterising the sea-water from which the ice was produced; that is to say, the value for D is greater in the water obtained by melting sea-water ice than in sea-water in which the ice originally formed.

There seems good reason to hope that by further investigation along the lines suggested in this brief abstract, it will be possible to trace to their origin the waters carried by different oceanic currents, and thereby to throw much light upon some of the most difficult and most important of oceanographic problems.

ON THE DISSOCIATION OF ELECTROLYTES IN SOLUTION AS SHOWN BY COLORIMETRIC DETERMINATIONS.

By H. M. VERNON, B.A.

(Concluded from p. 144).

The Relations of the Colours of Salts to One Another.

In addition to determining the changes of colour of salt solutions on dilution and on rise of temperature, the colours of the solutions of the different salts were compared against each other wherever possible. The normal solutions were generally compared. From the values so obtained, and from the values for the decrease of colour of the salts on dilution, the colour ratios at other dilutions can easily be calculated. In several cases the solutions were compared with each other at two dilutions as a test of the correctness of the colour comparisons. The experimental numbers agreed well with the calculated.

Base.	Colouration for—			
	Chloride.	Sulphate.	Nitrate.	Acetate.
Cupric.. ..	100	96.9	110.7	877.7
Nickel.. ..	100	87.8	81.1	—
Cobalt.. ..	100	78.1	71.8	—
Uranyl.. ..	100	142.2	68.4	51.0
Chromic.. ..	100	79.9	—	—
Ferric.. ..	100	—	—	2147.0

In most cases the other salts were compared directly with the chloride, but in the case of copper they were compared with the sulphate. Of cupric salts the normal solutions were compared, except in the case of the acetate when the 2.5 litre solution was used. The solution of this salt, it will be observed, is nearly eight times darker in colour than that of any other cupric salt. As has been shown, it also dissociates more on dilution than any other cupric salt. The probable reason of this is that copper acetate in its concentrated solutions is not dissociated to nearly so great an extent as any of the other salts, and therefore forms solutions of much darker colour, and also dissociates more on dilution. Thus Kohlrausch has shown (*Pogg. Ann.*, ciii., p. 35), that most sulphates, nitrates, and chlorides are more than half dissociated even in their normal solutions, whilst acetates are only slightly dissociated. Cupric nitrate solution shows the next greatest colour effect. The colour effect of copper chlorate solution was 85.2. The colour of the normal solution of the chloride was too greenish for accurate

comparison, so the decinormal solution, which had just the same tint as the other solutions, was compared, and the value for the normal solution calculated from this. With the exception of the chloride the solutions of all the cupric salts appeared to be of exactly the same shade of colour. The colour effect of the decinormal solution of the chlorate was found to be 83.6, the calculated value being 82.8.

Of nickel salts the chloride shows the greatest colour effect, then the sulphate, and then the nitrate. Solutions of the chloride were very slightly more yellowish in tinge than those of either the sulphate or nitrate. Cobalt salts show the same general relations to each other as nickel salts. The tint of the solution of the chloride was slightly more purple than that of the sulphate or nitrate. The decinormal cobalt nitrate solution was found to have the colour value 82.4, the calculated being 82.8. The uranium salt solutions compared were of 2.5 litre strength, and not normal. The value for the acetate is rather remarkable, as instead of being greater than those of the other salts, like copper acetate, it is much smaller than any of them. The value found for decinormal uranyl sulphate was 145.4, the calculated being 148.0. Of chromium salts only the sulphate and chloride could be compared, the alum being violet in colour and the nitrate brown. Only the decinormal solutions of these salts were compared, the normal being too dark in colour.

Ferric salts taken as a whole yielded very remarkable results. Thus the sulphate forms only slightly coloured solutions, so they could not be compared. Ferric ammonium citrate proved to give exceedingly dark solutions, the colour of the decinormal compared with that of decinormal ferric chloride taken as 100 being 378.0, or nearly forty times as dark. All the values of the ferric salts are calculated for decinormal solutions, as in some cases the normal solutions were too dark to be compared. With ferric acetate and ferric ammonium citrate even the decinormal solutions were too dark for accurate comparison, so 100 litre solutions were made use of, and the values calculated from the results obtained with these. The acetate gave the next highest colour value, viz., 2147.0. The value is thus very much greater than even that found for copper acetate. The value for ferric citrate was found to be about 550, and for ferric tartrate about 350.

As will be shown later on, no proper colour comparison is possible between the solutions of these salts. Ferric oxalate and acid ferric citrate solutions could not be compared, as they are greenish yellow in colour. Thus all the organic ferric salt solutions it was possible to examine had values very much greater than that of ferric chloride. The reason of this is probably the same as that given to account for the large colour value of copper acetate solution.

On endeavouring to compare solutions of neutral ferric chloride with those of acid ferric chloride, ferric tartrate, and ferric citrate, very peculiar results were obtained. Thus it was found that the relation of the volumes of these liquids required to produce the same tint varied according to the thickness of the layer of ferric chloride solution they were compared with.

In the following table are given the colour effects of layers, 1 to 3 c.m. in thickness, of solutions of each salt compared with layers of equal thickness of acid ferric chloride solution taken as 100.

Thickness of layer of solution in c.m.	Colour effect of solution of—		
	Ferric chloride.	Ferric tartrate.	Ferric citrate.
1	39.0	154.7	255.0
1.5	49.6	185.3	285.1
2	58.8	213.0	312.0
2.5	67.5	227.5	339.1
3	72.4	230.6	349.7

As former experiments showed that the colour effect of acid ferric chloride solution increases proportionately to

the thickness of the layer of liquid viewed, it follows that the colour effects of the solutions of these three salts increase in a greater proportion than that of the thickness of the layers. Thus a layer of ferric chloride solution 3 c.m. in thickness has a colour effect nearly six times as great as a layer 1 c.m. in thickness, instead of only three times as great. These variations must be in some way due to the presence of free ferric oxide in the solutions.

The above results show that ferric tartrate and ferric citrate solutions also contain considerable quantities of ferric oxide, though not nearly so much as neutral ferric chloride solution. As on comparing together solutions of neutral ferric chloride, ferric ammonium citrate, and ferric acetate, no variations depending on the thickness of the layers of liquid examined were noticed, it follows that solutions of these two salts must contain as large quantities of ferric oxide in suspension as those of neutral ferric chloride. Now ferric ammonium citrate solution was found to afford scarcely any change at all in colour effect on dilution. There are probably, therefore, two opposite changes going on within it at the same time on dilution; one, a decomposition with formation of ferric oxide and an increase of colour effect; the other, a partial dissociation of the salt into ferric citrate and ammonium citrate, attended by a great decrease of colour effect.

Of the other salt solutions examined none could be compared together but those of potassium bichromate and chromium trioxide. If the colour effect of decinormal potassium bichromate solution be taken as 100, that of chromium trioxide is 23.2, or less than a fourth as great. Taken as a whole we see that the colour effects of organic salts are the greatest, those of chlorides next, then those of sulphates, and lastly those of nitrates. The colour effects of salts bear a considerable resemblance to the decrease of colour their solutions undergo on dilution. Thus those of organic salts show the greatest decrease on dilution, with the exception of uranyl acetate solution, which shows less decrease than any of the uranyl salts, and also less colour effect. Ferric citrate and tartrate solutions are also exceptions, but, as has been shown, their increase in colour on dilution is due to the formation of ferric oxide. Chlorides, with the exception of cupric chloride, show the next greatest colour decrease on dilution of their solutions. Cupric nitrate solution, which shows a greater colour decrease on dilution than solutions of either the chloride or the sulphate, also possesses a greater colour effect than these two solutions.

Nitrate solutions show a slightly greater decrease than sulphate solutions, although their colour effects are rather smaller. This is even the case with uranyl nitrate, although the colour effect of the sulphate is twice as large. This, in fact, forms the only marked exception to the otherwise general resemblance. The resemblance is manifestly much too great to be due to mere chance, and there is every reason to suppose it is due to the solutions with a greater colour effect containing the salts in a less dissociated state than those with a less colour effect, so that on dilution they decrease in colour effect or undergo dissociation to a greater degree.

The study of the colourimetric relations of solutions of salts at various dilutions and temperatures has thus been shown to give support to the electrolytic dissociation theory on the one hand, and to the hydrate theory on the other. Inasmuch as many and distinct proofs of the correctness of both these different theories on the nature of solution have been advanced, and as at first sight they appeared to be totally contrary to one another, the supporters of each theory tended rather to the opinion that the theory of the opposite party was quite incorrect. It is hoped that these experiments may be taken to indicate the possibility of both theories being correct. It would seem, therefore, that whilst salts in hot or very concentrated solutions exist in great part as anhydrous molecules, or as hydrates containing only small numbers of water molecules, they are also to a certain extent dissociated into their ions. In moderately dilute solutions

they are more dissociated, and at the same time the hydrates present contain more water molecules. In very dilute solutions the salts are totally dissociated into their ions, and no hydrates exist at all in solution. There is every probability that hydrates are completely decomposed at extremely dilute solutions, for it is evident that as a solution gets more and more dilute, and the hydrates in it contain more and more water molecules, the bonds which hold the salt molecule to the water molecules must become more and more feeble, till at last they dwindle down to nothing, and so the hydrates no longer have an existence.

Summary.

The chief conclusions arrived at in this paper are as follow:—

1. Almost all the solutions of the thirty-five coloured salts examined show considerable decrease in colour effect on dilution, due in all probability to dissociation taking place. The only exceptions are certain chromium derivatives, the colour of whose solutions, on gradual dilution, either remains constant or increases slightly. When their solutions are suddenly diluted, different colour values are obtained. Potassium permanganate solution only shows a very slight decrease in colour on dilution. Taken as a whole ferric salts show the greatest decrease in colour effect on dilution of their solutions, then cobalt salts, then uranium salts, and then nickel and cupric salts. Generally also organic salts show the most decrease of colour on dilution, chlorides less, nitrates still less, and sulphates the least.

2. All solutions of salts, with the exception of those of certain chromium derivatives, and perhaps of potassium permanganate, increase considerably in colour effect on being heated. The amount of colour increase depends on (1) the nature of the base of the salt, ferric salt solutions being most affected by temperature, then those of cobalt and uranium, and then those of copper and nickel; (2) on the nature of the acid radicle, chlorides being most affected, nitrates next, and sulphates least; (3) on the degree of dilution of the solution, sulphates being most affected in their decinormal solutions and least in their centinormal, whilst chlorides are most affected in their normal solutions and least in their centinormal. The results obtained for the effect of temperature on the colours of salt solutions are without exception in favour of the hydrate theory of the nature of solution.

3. On comparing solutions of different salts together as to colour effect, it is found that the values obtained bear considerable resemblance to the amounts of decrease of colour the solutions undergo on dilution, organic salts possessing the greatest colour effect, chlorides a lesser effect, sulphates and nitrates a still smaller colour effect. The results obtained as a whole indicate that dissociation takes place in solutions on the one hand, and hydrates are formed on the other, so it would seem that salts exist in solution in both these conditions at the same time.

ON AN APPARENT RELATION OF ELECTROMOTIVE FORCE TO GRAVITY.*

By Dr. G. GORE, F.R.S.

IN a research on "A General Relation of Electromotive Force to Equivalent Volume and Molecular Velocity of Substances" (*Proc. Birm. Phil. Soc.*, 1892, vol. viii., pp. 63—138; *Electrical Review*, vol. xxx., pp. 693, 722, 755, 786), I have demonstrated, by means of a large number and variety of experimental measurements, that the dilution of the liquid of a voltaic cell by means of water or alcohol, the solution of either the positive metal or the

negative one by means of mercury, the dilution of either of these amalgams by means of mercury, or the dilution of one solid metal by means of another in an alloy, is universally attended by an increase of mean electromotive force of the diluted and diluting substances beyond the calculated amount, and therefore of the actual electromotive force of the diluted one (that of the diluent being very little affected), provided that no chemical union of the diluted and diluting substances occurs. If, however, chemical union does occur, this gain of electromotive force is diminished, or converted into a loss which is larger in proportion as the union is more intimate.

In these experiments, by the act of solution or dilution, the molecules of the active or diluted substance are separated farther apart by those of the neutral or diluting one, and acquire greater freedom of motion, whilst those of the diluent approach only slightly nearer together, and do not perceptibly affect the result.

It is generally admitted that the particles of all bodies are in an incessant state of motion, that this motion is the *vis viva* or energy contained in the substance, and that the laws of motion apply equally to the smallest as to the largest bodies. If now we regard each molecule of the active substance as vibrating like a pendulum, its movements must obey the law of falling bodies, and the larger the degree of freedom of motion the greater the arc of vibration, the larger the fall, and the greater the velocity of motion. And, as in the above mentioned experiments the volta electromotive force of substances generally has been proved to vary directly as the degree of molecular freedom, it must also, according to this view, be directly related to, and dependent upon, the velocity of molecular motion and the law of gravity in the above manner.

A METHOD FOR THE DETERMINATION OF BARIUM IN THE PRESENCE OF CALCIUM AND MAGNESIUM.*

By F. W. MAR.

THE recent investigation by Prof. R. Fresenius (*Zeit. f. Anal. Chem.*, xxx., 595) of the value of the various methods which have been proposed for the separation of barium and calcium, shows that but two of the methods tested by him are sufficiently accurate for good analytical work, and even with these it is necessary to make two treatments in order to obtain a complete separation. The method here described may therefore be of interest, and, by reason of its rapidity and accuracy, may prove valuable, although since the publication of the work of Fresenius another method (P. E. Browning, *Am. Jour. Sci.*, xliii., p. 314) has been published from this laboratory which, in point of accuracy, leaves little to be desired.

It has long been known that barium chloride is insoluble to a marked degree in concentrated hydrochloric acid, but the difficulty of filtering off the strong acid has in the past prevented the determination of the exact amount of this insolubility, and for the same reason the reaction has not been available for quantitative use. Since the invention of the Gooch crucible, however, the treatment of such strong acid filtrates has become a matter of the greatest ease, and it seemed worth while to investigate the limits of the insolubility of barium chloride in the strong acid and to ascertain whether the reaction might not be of use in the separation of barium from calcium and magnesium, the chlorides of which are soluble in the strong acid.

The barium chloride used in the following experiments was the pure crystallised chloride containing two molecules of water. The calcium salt was the pure fused chloride, and the magnesium salt was the pure crystal-

* From the *Philosophical Magazine* for September, 1892.

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xliii., June, 1892.

lised magnesium chloride dried at 50° C. As the two latter were not determined in the experiments it was not necessary to know the composition of the salts used as regards hygroscopic moisture. Attention was first given to determining the solubility of barium chloride in hydrochloric acid.

Series A.

Exp.	BaCl ₂ .2H ₂ O. Grm.	Water. C.m.s	HCl. C.m.s	Total filtrate. C.m.s	BaCl ₂ . Grm.	Loss. Grm.
1.	0.5024	5	20	—	0.4241	0.0041
2.	0.5084	5	20	—	0.4304	0.0030
3.	0.5099	2	25	—	0.4320	0.0027
4.	0.5033	2	25	90	0.4251	0.0039
5.	0.5047	2	25	52	0.4247	0.0055
6.	0.5065	2	50	115	0.4257	0.0060
7.	0.5008	2	50	75	0.4218	0.0051
8.	0.5011	2	50	93	0.4220	0.0051
9.	0.5024	2	75	123	0.4246	0.0037

The experiments in Series A were made as follows:—The barium salt was weighed out, placed in a small beaker, and dissolved in the amount of water indicated. The barium was then precipitated as the anhydrous chloride by adding, gradually at first, the amount of hydrochloric acid shown. After standing for five or ten minutes the precipitates were filtered off upon asbestos in Gooch crucibles, washed with concentrated hydrochloric acid, dried sometimes over a low flame (at about 150°—200° C.) and sometimes in an air bath heated to 165° C., and weighed. In several cases the total filtrate was measured and the volume is given in the tabular statement. The results show a considerable solubility amounting to about 1 part in 8000 under the conditions given.

Series B.

Exp.	BaCl ₂ .2H ₂ O. Grm.	Water. C.m.s	HCl. C.m.s	Total filtrate. C.m.s	BaCl ₂ . Grm.	Loss. Grm.
10.	0.5057	2	25	75	0.4268	0.0042
11.	0.5017	5	50	90	0.4198	0.0078
12.	0.5068	3	50	100	0.4235	0.0085
13.	0.5019	2	100	144	0.4186	0.0082

The experiments in Series B were conducted similarly to those of Series A, except that the precipitates were allowed to stand twenty-four hours before filtration. The loss due to solubility was, as is shown by the table, greater than before, due doubtless to the escape of hydrochloric acid gas from the solution.

Series C.

Exp.	BaCl ₂ .2H ₂ O. Grm.	Water. C.m.s	HCl. C.m.s	Alcohol. C.m.s	BaCl ₂ . Grm.	Loss. Grm.
14.	0.5011	3	25	15	0.4228	0.0043
15.	0.5096	2	25	10	0.4278	0.0066

The experiments of Series C were conducted in the same manner as those of Series A, except that the amount of absolute alcohol indicated was added after the precipitation by hydrochloric acid. The results show that the alcohol neither decreased nor increased the amount of the solubility of the chloride.

Series D.

Exp.	BaCl ₂ .2H ₂ O. Grm.	HCl. C.m.s	BaCl ₂ . Grm.	Loss. Grm.
16.	0.5019	50	0.4249	0.0029
17.	0.5020	50	0.4257	0.0022
18.	0.5020	50	0.4255	0.0024
19.	0.5016	50	0.4259	0.0017
20.	0.5022	50	0.4267	0.0014

In the experiments of Series D the weighed barium chloride was placed in an Erlenmeyer beaker and dissolved in 4 or 5 c.c. of water. The indicated amount of acid was then added, and a stream of hydrochloric acid gas was passed for two hours into the cooled mixture. The precipitates were then treated as in the former experi-

ments. The results show that even in the strongest possible solution, at the ordinary temperature, of hydrochloric acid barium chloride is soluble to a considerable degree, this solubility amounting according to the first three experiments of the series to about one part in 20,000. In Experiments 18 and 19 ten c.c. of absolute ether were added to the solution before passing in the hydrochloric acid gas. The results showed that the ether seemed to decrease the solubility of the barium salt, and therefore the experiments of the following series were undertaken.

Series E.

Exp.	BaCl ₂ .2H ₂ O. Grm.	HCl. C.m.s	Ether. C.m.s	BaCl ₂ . Grm.	Loss. Grm.
21.	0.5008	50	10	0.4267	0.0002
22.	0.5002	50	10	0.4257	0.0007
23.	0.4999	50	10	0.4252	0.0009
24.	0.4999	50	10	0.4258	0.0003
25.	0.5003	25	25	0.4259	0.0005
26.	0.5002	25	5	0.4262	0.0002
27.	0.5099	25	5	0.4344	0.0003
28.	0.5003	25	5	0.4261	0.0003

The experiments of Series E were conducted as follows. The amount of barium salt specified was dissolved in the least convenient amount of hot water (about 2 c.m.s) and precipitation was brought about by adding the indicated amount of concentrated hydrochloric acid. The beaker containing the precipitate was then placed in cold water and the amount of ether shown in the tables was added and mixed with the solution by thorough stirring. After standing for five or ten minutes the precipitate was filtered off and washed with concentrated hydrochloric acid containing about ten percentum by volume of absolute ether and dried, sometimes in an air-bath at 165°—170° C. and at others over a radiator giving a temperature of 175°—200° C. A constant weight was more quickly obtained by the latter method, and it was used exclusively in the experiments of the subsequent series. In using it a low heat was used at first and the temperature was not increased until the precipitate was moderately dry. The results show that barium chloride is practically insoluble in a mixture of hydrochloric acid and ether containing about one-sixth by volume of the latter. The average solubility calculated from the experiments given is one part in 122,000. The actual solubility is less than this, since no account was taken of the volume of the washings, which were at least equal to the original filtrates.

Series F.

Exp.	BaCl ₂ .2H ₂ O. Grm.	CaCl ₂ . Grm.	HCl. C.m.s	Ether. C.m.s	BaCl ₂ . Grm.	Loss. Grm.
29.	0.5001	0.5	50	10	0.4250	0.0013
30.	0.4999	0.5	50	10	0.4250	0.0011
31.	0.5005	0.5	25	25	0.4260	0.0006
32.	0.5002	0.42	25	5	0.4258	0.0004
33.	0.5001	0.5	25	5	0.4255	0.0008
34.	0.5005	0.5	25	5	0.4251	0.0015
35.	0.5001	0.5	25	5	0.4254	0.0009
36.	0.5001	0.5	25	5	0.4258	0.0005
37.	0.5003	0.5	25	5	0.4261	0.0004
38.	0.1002	3.0	25	5	0.0842	0.0010
39.	0.0107	3.0	25	5	0.0080	0.0005
40.	0.5100	0.5	25	5	0.4328	0.0020

Series F was undertaken to test whether the mode of precipitating barium used in the preceding series would be of use in the separation of the barium from calcium. The experiments were conducted as in Series E, except that the calcium salt was dissolved with the barium chloride. It was necessary to use more water than in Series E to effect solution, but as the barium salt was uniformly the last to dissolve, the effect was practically the same as before. The results show that mixtures of barium and calcium in all proportions are perfectly sepa-

rated by this method, 0.0000 grm. of barium chloride being separated with accuracy from 3 grms. of calcium chloride. The calcium does not show the slightest tendency to come down with the barium, and those experiments in which separation was effected by the use of 25 c.m.³ of hydrochloric acid and 5 c.m.³ of ether gave rather better results than those in which double this volume was employed. It is better not to let the precipitations stand too long before filtration, even if kept cold, as the hydrochloric acid evaporates from the solution, and experiments in which filtration was delayed for about two hours (e.g., Experiments 33, 34, 35) show a rather larger loss than the average. That there is no advantage in increasing the amount of ether over the proportions used above is shown by Experiment 31, which is comparable with Experiment 25. In the case of Experiment 40, in which no ether was used, the result is comparable with the experiments of Series A. The precipitate was washed, however, with the mixture of hydrochloric acid and ether.

Series G.

Exp.	BaCl ₂ .2H ₂ O. Grm.	MgCl ₂ .6H ₂ O. Grm.	HCl. C.m. ³	Ether. C.m. ³	BaCl ₂ . Grm.	Loss. Grm.
41.	0.4999	0.5	25	5	0.4253	0.0007
42.	0.5000	0.5	25	5	0.4257	0.0005
43.	0.1002	3.0	25	5	0.0844	0.0008
45.	0.0100	3.0	25	5	0.0077	0.0008

The experiments of Series G were made in exactly the same manner as those of Series F, except that varying amounts of magnesium chloride were present instead of the calcium salt. The results are uniform and exact, and indicate that barium may be separated from magnesium when the two are present in any proportion. It is probable that if magnesium chloride were present in an amount larger than 3 grms. in 30 c.m.³, it would be necessary to make two treatments, as under those circumstances it shows a slight tendency to precipitate. The amount of mixed salts present should always, therefore, be kept below this limit.

Recapitulation.—Barium chloride is soluble to an extent not exceeding one part in 20,000 in pure concentrated hydrochloric acid, but the solubility increases very rapidly with the diminution in the strength of the acid. In concentrated hydrochloric acid containing ether it is soluble to an amount not exceeding one part in about 120,000. To utilise this fact for the separation of barium from calcium and magnesium, the chlorides of the earths are dissolved in the least possible amount of boiling water, and precipitated by 25 c.m.³ of concentrated hydrochloric acid, with the addition of 5 c.m.³ of absolute ether after cooling. The acid should be added drop by drop, at first allowing the precipitate formed to re-dissolve as long as possible, as the precipitate is thus obtained in a coarse crystalline condition and filters very quickly, and is less liable to include foreign matter. After standing a few minutes the precipitate is to be filtered in a Gooch crucible, washed with hydrochloric acid containing about 10 per cent of ether, and dried at 150°–200° C. The method is accurate and rapid, and possesses the further advantage when a number of determinations are to be made that the precipitate may be dissolved off of the felt by a little water, and, after ignition, the crucible and felt may be used again without re-weighing. A felt upon which half a dozen precipitates were weighed did not change its weight to the extent of one-tenth of a mgrm. The fumes of the strong acid cause no inconvenience if the filtration is performed in front of a good flue. A gas flame may be used in the flue without danger from the ether, which seems to be firmly held by the hydrochloric acid. A flame was used to increase the draught in all of the experiments given, and with entire safety, even when the filtrate contained 50 per cent by volume of ether.

The author wishes in concluding to acknowledge his indebtedness to Prof. Gooch for many helpful suggestions freely given in the course of the investigation.

NOTES ON THE ANALYSIS OF THE
NITRO-EXPLOSIVES.*

By P. GERALD SANFORD, F.I.C., F.C.S.

Now that the various forms of nitro compounds are gradually replacing the older forms of explosive agents, both for blasting purposes and also as a propulsive agent, perhaps some notes upon the methods for their analysis and examination, that I have used and found to work satisfactorily, may be of service to other chemists who may be engaged upon similar work. The class of compounds that have come into the most extended use for the purposes of mining, blasting, &c., are the nitro-glycerin compounds, more especially the gelatin compounds, composed of nitro-cellulose and nitro-glycerin, and generally containing some admixture of nitrates and wood pulp, or similar materials.

Kieselguhr Dynamite.

This material generally consists of 75 per cent nitro-glycerin and 25 per cent of the infusorial earth Kieselguhr. The analysis is very simple, and may be conducted as follows:—Weigh out about 10 grms. of the substance, and place over calcium chloride, in a desiccator, for some six to eight days, and then re-weigh; the loss in weight gives the moisture; this will generally be very small, probably never more than 1 per cent. The dry substance may now be wrapped in filter-paper, the whole weighed, and the nitro-glycerin extracted in the Soxhlet apparatus with ether. The ether should be distilled over at least twenty-four times. I have found, however, that results may be obtained much quicker, and quite as accurate, by leaving the dynamite in contact with ether in a small Erlenmeyer flask for some hours,—leaving it over night is better,—and then decanting, and again allowing the substance to remain in contact with the ether for a few hours, and finally filtering through a weighed filter, drying at 100° C., and weighing. This gives the weight of Kieselguhr. The nitro-glycerin must be obtained by difference, as it is quite useless to evaporate down the ethereal solution to obtain it, as it is itself volatile to a very considerable extent at the temperature of evaporation of the ether, and the result, therefore, will always be much too low. An actual analysis of Kieselguhr dynamite gave:—Moisture, 0.92 per cent; Kieselguhr, 26.15 per cent; and nitro glycerin, 72.93 per cent, this last being obtained by difference.

Gelatin Compounds.

The simplest of these compounds is, of course, blasting gelatin, as it consists of nothing but nitro-cotton and nitro glycerin, the cotton being dissolved in the glycerin to form a clear jelly, the usual proportions being about 92 per cent of nitro glycerin to 8 per cent of nitro-cotton, but the cotton is found as high as 10 per cent in some gelatins. Gelatin dynamite and gelignite are blasting gelatins with varying proportions of wood pulp and saltpetre (KNO₃), mixed with a thin blasting gelatin. The method of analysis is as follows:—Weigh out about 10 grms. of the substance, previously cut up in small pieces, and place over calcium chloride in a desiccator for some days. Re-weigh; the loss equals moisture. This is generally very small. The dried sample is then transferred to a small thistle-headed funnel which has been cut off from its stem, and the opening plugged with a little glass wool, and round the top rim of which a piece of fine platinum wire has been fastened, in order that it may afterwards be easily removed from the Soxhlet tube. The weight of this funnel and the glass wool must be accurately known. It is then transferred to the Soxhlet tube and exhausted with ether, which dissolves out the nitro-glycerin. The weighed residue must afterwards be

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treated with ether-alcohol to dissolve out the nitro-cotton.

But the more expeditious method is, perhaps, to transfer the dried gelatin to a conical Erlenmeyer flask of about 500 c.c. capacity, and add 250 c.c. of a mixture of ether-alcohol (2 ether to 1 alcohol), and allow to stand over night. (Sometimes a further addition of ether-alcohol is necessary, but not often). The undissolved portion, which consists of the wood pulp, and potassium nitrate, and other salts, is then filtered off, dried, and weighed.

Solution.—The ether-alcohol solution contains the nitro-cotton and the nitro-glycerin in solution. To this solution add excess of chloroform, when the nitro-cellulose will be precipitated in a gelatinous form. This should be filtered off through a linen filter, and allowed to drain. It is useless to attempt to use a filter pump, as it generally causes it to set solid. The precipitated cotton should then be re-dissolved in ether-alcohol, and again precipitated with excess of chloroform. This precaution is absolutely necessary, as otherwise the results will be much too high, owing to the gelatinous precipitate retaining very considerable quantities of nitro-glycerin. The precipitate is then allowed to drain as completely as possible, and finally dried in the air-bath at 40° C. until it is easily detached from the linen filter by the aid of a spatula, and then transferred to a weighed watch-glass, replaced in the oven, and dried at 40° until constant in weight. The weight found, calculated upon the 10 grms. taken, gives the percentage of nitro cellulose.

The residue left after treating the gelatin with ether-alcohol is, in the case of blasting gelatin, very small, and will probably consist of carbonate of soda. It should be dried at 40° C., and weighed, but in the case of either gelignite or gelatin dynamite this residue should be transferred to a beaker and boiled with distilled water, and the water decanted three or four times, and the residue finally transferred to a tared filter and washed for some time with hot water. The residue left upon the filter is wood pulp. This is carefully dried at 40° C., until constant, and weighed. The solution and washings from the wood are evaporated down in a platinum dish and dried at 100° C. in the oven, and weighed. It will consist of the potassium nitrate, and any other mineral salts, such as carbonate of soda, which should always be tested for by adding a few drops of nitric acid and a little water to the residue, and again evaporating to dryness and re-weighing. From the difference in weight the soda can be calculated, sodium nitrate having been formed.

The nitro-glycerin is best found by difference, but, if desired, the solutions from the precipitation of the nitro-cellulose may be evaporated down upon the water-bath at 30° to 40° C., and finally dried over CaCl_2 until no smell of ether can be detected, and the nitro-glycerin weighed. It will, however, always be much too low. An actual analysis of a sample of gelatin dynamite gave the following result:—

Nitro-cellulose	3.819 per cent.
Nitro-glycerin	66.691 "
Wood pulp	16.260 "
KNO_3	12.890 "
Water	0.340 "

100.000

This sample was probably intended to contain 30 per cent of absorbing material to 70 per cent of explosive substances.

Gun-Cotton.—Collodion cotton, and other forms of nitro-cellulose, i.e., the hexa-nitro-cellulose and lower nitro bodies. The first thing upon opening a case of wet gun-cotton, or in receiving a sample from "the poacher," that requires to be determined, is the percentage of water that it contains; it is best done by weighing out about 1000 grms. upon a paper tray, which has been previously dried in the oven at 100° C. for some time and become

constant in weight. The tray full of cotton is then placed in a water oven, kept at 100° C., and dried as long as it loses water. The loss gives the percentage of water. It varies from 20 to 30 per cent, as a rule, in what is known as wet cotton.

The Solubility Test.—The object of this test is to ascertain, in the case of gun-cotton, the percentage of soluble (penta and lower nitrates) cotton that it contains, or, in the case of soluble cotton, the quantity of gun-cotton. The method of procedure is as follows:—Five grms. of the sample, which has been previously dried at 100° C. and afterwards exposed to the air for two hours, is transferred to a conical flask, and 250 c.c. of ether-alcohol added. The flask is then corked and allowed to digest, with repeated shaking, for two or three hours. The whole is then transferred to a linen filter, and, when the solution has passed through, the filter is washed with a little ether and pressed in a screw-press between folds of filter-paper. The sample is then returned to the flask, and the previous treatment repeated, but it will be sufficient for it to digest one hour the second time. The filter is then opened up, and the ether allowed to evaporate. The gun-cotton is then removed from the filter and transferred to a watch-glass, and dried in the water oven at 100° C. When it is dry it is exposed to the air for two hours and weighed. It equals the amount of gun-cotton and unconverted cotton. In the 5 grms. the non-nitrated cellulose must be determined in a separate 5 grms. and deducted.

Estimation of the Non-nitrated Cotton.

However well the cotton has been nitrated, it is almost certain to contain a small quantity of non-nitrated or unconverted cotton. This can be determined thus:—Five grms. of the sample are boiled with a saturated solution of sodium sulphide, and then allowed to stand for forty-eight hours, and afterwards filtered or decanted, and again boiled with fresh solution of sulphide, and again filtered, dried, and weighed. The residue is the cellulose that was not nitrated. It should be ignited, and the weight of the ash deducted from the previous weight.

Alkalinity.

Five grms. of the air-dried and very finely divided sample are taken from the centre of the slabs or discs, and digested with about 20 c.c. of $\frac{N}{2}$ hydrochloric acid, and diluted with water to about 250 c.c., and shaken for about fifteen minutes. The liquid is then decanted and washed with water until the washings no longer give an acid reaction. The solution, together with the washings, are then titrated with $\frac{N}{2}$ sodium carbonate, using litmus as indicator.

Nitrogen.

The estimation of the percentage of nitrogen in a sample of gun-cotton or collodion cotton is perhaps of more value, and affords a better idea of its purity and composition than any of the foregoing methods of examination, and, taken in conjunction with the solubility test, it will generally give the analyst a very fair idea of the composition of his sample. If we regard gun-cotton as the hexa-nitro-cellulose $\text{C}_{12}\text{H}_7\text{O}_4(\text{ONO}_2)_6$, the theoretical amount of nitrogen required for the formula is 14.14 per cent; and in the same way for collodion cotton, which consists of the lower nitrates, that is the penta and tetra-nitro bodies, the theoretical nitrogen is 11.11 per cent and 6.76 per cent respectively; so that, if in a sample of gun-cotton the nitrogen falls much lower than 14 per cent, it probably contains considerable quantities of the lower nitrates, and perhaps some non-nitrated cellulose as well ($\text{C}_6\text{H}_{10}\text{O}_5$), which, of course, would also lower the percentage of nitrogen. The most expeditious method of determining the nitrogen in these nitro-bodies is by the use of Lunge's nitrometer, and the best way of working the process is as follows:—Weigh out with the greatest care 0.6 gm. of the previously dried cotton in a

small weighing bottle of about 15 c.c. capacity, and carefully add 10 c.c. of concentrated sulphuric acid from a pipette. Allow to stand until all the cotton is dissolved. The nitrometer should be of a capacity of 150 to 200 c.c., and should contain a bulb of 100 c.c. capacity at the top, and should be fitted with a Greiner and Friederich's three-way tap. When the nitro-cotton has entirely dissolved to a clear solution, raise the pressure of the nitrometer, so as to bring the mercury in the measuring tube close up to the tap. Open the tap, in order to allow of the escape of any air-bubbles, and clean the surface of the mercury and the inside of the cup with a small piece of filter-paper. Now close the tap, and pour the solution of the nitro-cotton into the cup. Rinse out the bottle with 15 c.c. of concentrated sulphuric acid, contained in a pipette, pouring a little of the acid over the stopper of the weighing bottle, in case some of the solution may be on it. Now lower the pressure tube a little, just enough to cause the solution to flow into the bulb of the measuring tube when the tap is slightly opened. When the solution has run in almost to the end, turn off the tap, wash down the sides of the bottle, and add to the cup of the nitrometer; allow it to flow in as before, and then wash down the sides of the cup with 10 c.c. of sulphuric acid, adding little by little, and allowing each portion added to flow into the bulb of the nitrometer before adding the next portion. Great care is necessary to prevent air-bubbles obtaining admission, and if the pressure tube is lowered too far the acid will run in with a rush and carry air along with it. The solution being all in the measuring tube, the pressure tube is again slightly raised, and the tube containing the nitro-cotton solution shaken for ten minutes with considerable violence. It is then replaced in the clamp, and the pressure relieved by lowering the pressure tube, and the whole apparatus allowed to stand for twenty minutes, in order to allow the gas evolved to assume the temperature of the room. A thermometer should be hung up close to the bulb of the measuring tube. At the end of the twenty minutes the levels of the mercury in the pressure and measuring tubes are equalised, allowing about three inches of the sulphuric acid to one inch of mercury, and the final adjustment obtained by slightly opening the tap on the measuring tube (very slightly), after first adding a little sulphuric acid to the cup, and observing whether the acid runs in or moves up. This must be done with very great care. When accurately adjusted it should move neither way. Now read off the volume of the NO gas in c.c. from the measuring tube. Read also the thermometer suspended near the bulb, and take the height of the barometer in millimetres. The calculation is very simple.

Example Collodion Cotton.

0.6 grm. taken. Reading on measuring tube = 114.6 c.c. NO. Barometer, 750 m.m. Temperature, 15° C.

Since 1 c.c. NO = 0.6272 grm. N., and correcting for temperature and pressure by the formula $760 \times (1 + d^2)$ ($d = 0.003665$) for temperature of 15° = 801.78; then—

$$\frac{114.6 \times 100 \times 750 \times 0.6272}{801.78 \times 0.6} = 11.22 \text{ per cent N.}$$

Theory = 11.11 per cent for $C_6H_8(NO_2)_2O_5$.

The following is the analysis of a good sample of collodion cotton suitable for the manufacture of blasting gelatin, &c.

Soluble cotton	= 99.118 p.c.	} = Nitrogen = 11.67 p.c.
Gun cotton	= 0.642 "	
Non nitrated cotton	= 0.240 "	

The nitrogen in nitro-glycerin may, of course, be determined by the nitrometer, but in this case it is better to take a much smaller quantity of the substance,—from 0.1 to 0.2 grm. is quite sufficient. This will give from 30 to 60 c.c. of gas, and therefore a measuring tube without a 100 c.c. bulb must be used.

Example.

0.1048 grm. nitro-glycerin taken; Barometer, 761 m.m.; Temperature, 15° C.; gave 32.5 c.c. NO.

$$\frac{32.5 \times 100 \times 761 \times 0.6272}{801.78 \times 0.1048} = 18.46 \text{ per cent N.}$$

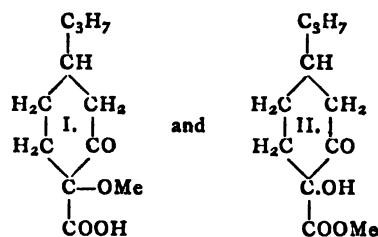
Theory for $C_{13}H_{14}O_4(ONO_2)_6 = 18.50 \text{ per cent.}$

METHYL SALTS OF CAMPHORIC ACID.*

By JAMES WALKER, Ph.D., D.Sc.

THE author prepared the two isomeric hydrogen methyl camphorates, and investigated their electrolytic conductivity with a view to testing the validity of Friedel's formula for camphoric acid. The substances he obtained are identical with those prepared by Brühl.

According to Friedel, camphoric acid forms two hydrogen methyl salts having the formulæ—



Now these substances ought to be widely different in their strength as acids, and consequently in their dissociation constants as determined from the electrolytic conductivity of their solutions. I. should have a constant greater than that of camphoric acid itself, while II. should have a constant ten times less at least than that of camphoric acid. As a matter of fact, the constants of the two isomeric substances are very nearly the same, and equal to about half the constant of camphoric acid, which is precisely what should be expected if camphoric acid were a dicarboxyl acid (compare Walker, *Journ. Chem. Soc.*, 1892, p. 715).

THE RED CHALKS OF ENGLAND.

By WILLIAM JOHNSTONE,
Emeritus Fellow of the Institute of Chemistry.

HAVING had occasion some time ago to make a number of analysis of the English chalks, both white and red, and as I know they will be of interest to several of your readers, I append the results obtained from the red chalks of Yorkshire, reserving for a future communication those of Norfolk.

No. 1.—From Speeton Gap. From top red bed, 3 ins. to 2 ft. 8 ins. thick.

No. 4.—From Speeton Gap. From upper of lower red beds.

No. 5.—From Speeton Gap. From lower of lower red beds.

No. 8.—From Warter. From Gravel Pit.

No. 10.—From Millington. From Millington Wolds.

No. 13.—From Speeton Cliff. From Red Marl Bed.

No. 15.—From Speeton Cliff. From upper of lower red beds.

I have to thank my assistants, Messrs. H. E. Lindley, E. J. Philbrick, J. J. Hogg, and C. R. Lidgy, for assistance in the work.

* Read before the British Association, Edinburgh Meeting, 1892, Section B.

	No. 1.	No. 4.	No. 5.	No. 8.	No. 10.	No. 13.	No. 15.
SiO ₂	10'01	12'42	30'00	6'08	7'27	39'94	5'48
Fe ₂ O ₃	2'35	3'95	6'50	3'50	4'10	3'75	0'95
Al ₂ O ₃	1'60	2'07	2'35	1'25	2'50	2'67	0'65
MnO	trace	trace	trace	trace	0'62	1'20	trace
CaCO ₃	80'59	79'87	60'21	86'37	80'89	48'31	88'78
CaSO ₄	3'78	0'84	0'24	0'76	2'64	1'40	3'14
MgCO ₃	1'63	0'75	0'43	1'06	1'44	1'53	trace
	99'96	99'90	99'74	99'02	99'46	98 80	99'00

NOTICES OF BOOKS.

On the Organisation of Science; being an Essay towards Systematisation. By "A FREE LANCE." "Divide et Impera." London: Williams and Norgate.

We have here a pithy and timely pamphlet. The "Free Lance" touches with the point of his weapon certain flaws in our present system—or, as he happily calls it, *unsystem*—of the cultivation of science, and gives suggestions for their removal. To give no scope for misunderstanding, we must premise that our author is not dealing with *education*. He is scrutinising our facilities for the further cultivation of science by those who are no longer pupils in the ordinary sense of the term, but have entered upon a career of research. He points out that they find in their way a number of difficulties which are capable of removal, but which in the meantime waste the opportunities and the resources of the aspirant.

These difficulties, which are donkeys, if not lions, in the way, are to be found in our scientific societies and our scientific journals. Instead of having "a place for everything, and everything in its place," we have for many a thing, if not for everything, several places.

Now, let us suppose a young *savant* desirous of taking up some particular subject. His first and most obvious task is to ascertain what, if anything, has been previously done in this direction. If he neglect this tedious duty he may simply be wasting his time and inditing an *Ilias post Homerum*; or he may fall into unintentional plagiarism, and may involve his colleagues in an "unerquicklich"—as the Germans call it—controversy on priority. Now to ascertain what has been already published—say, on a chemical subject—in England alone he will have to wade through the journals of the Chemical Society, possibly the *Philosophical Transactions*, as well as the *CHEMICAL NEWS*, the *Analyst*, the publications of the Society of Chemical Industry, the *Chemical Trades' Journal*, the *Pharmaceutical Journal*, the *Chemist and Druggist*, &c. All this means both time and money—requisites with which the inquirer is not always over-burdened.

As regards biology, the case is still worse, as we have not here space to show. "A Free Lance" therefore proposes—if we understand him aright—a decrease in the number of societies, and a restriction on the class of subjects admitted by each. He takes up his parable against the Zoological and the Entomological Societies as "robbing" the Linnean. Possibly our author knows the circumstances which led to the formation of the Entomological Society. It was felt as a grievance that the Linnean Society was too exclusively botanical, and the Zoological Society too vertebrate, and as the Articulata form, in number of species, the vast majority of the animal kingdom, if not of the entire organic world, and as they are more powerful for good and evil than the other zoological divisions, it was felt that entomology was fully entitled to an organisation of its own. The author's remarks on the "collectors"—especially of so-called "British"—are fully justified.

Upon the conduct of the Microscopical Society, "A Free Lance" might, without injustice, have spoken more emphatically. It is a case of "cross divisions." We have no right to classify Nature according to the instruments which we use in the study of her different departments.

Would it be wise to institute a Spectroscopical Society, or a Blowpipe Society?

Some of the author's strictures must at once be accepted as too well founded. Our recognised scientific societies would doubtless become more energetic if country members were allowed to take part in the election of council and officers by sending in their ballot-papers by post. Another point which he notices with disapproval is the very perfunctory character of the discussion. He suggests as a remedy that papers should be printed and distributed among the Fellows before being read. This, we must add, is done very successfully by the Victoria Institute.

On one important point the author does not touch. Not the least important step required towards the organisation of science is the dissociation of the so-called "Literary and Philosophical" societies of our large provincial cities. Here science is to a great extent crowded out by a medley of matter which is included under the name of literature, and which appropriates so large a share of time at the society's meetings, and of the space in its "Proceedings," that it would be to the advantage of science to dissolve partnership.

How sound are the views of "A Free Lance" will be seen from the following passage:—"I am concerned here with the intellectual feeding—or starving—of not the professional scientists only, but of that whole body of educated—really educated—outsiders that we may anticipate will presently exist when our 'educational' establishments shall have left off teaching Latin verse and Greek myths and instituted a scientific culture."

Space does not permit us to discuss all the many utterances in this pamphlet which merit careful consideration, but we trust it will be widely and thoughtfully read.

A Handy Book for Brewers; being a Practical Guide to the Art of Brewing and Maltng, embracing the Conclusions of Modern Research which bear upon the Practice of Brewing. By HERBERT EDWARDS WRIGHT, M.A., author of "The Handbook for Young Brewers." London: Crosby Lockwood and Son, 1892.

To brewers of the olden time this book would seem an unintelligible curiosity. They were accustomed to obtain their results—intermingled, doubtless, with disastrous failures—by "rule of thumb." The experience of the observant brewer, backed by the traditions of the trade, was often a very safe guide to success, so long—but only so long—as all working conditions remained absolutely unaltered. But here was the difficulty. The quality of the water might change; the hops, even if always selected of one growth, might vary from season to season. But probably of all the materials used in industry yeast is the most mutable. It is only quite of late, as the result of a long and difficult course of microscopical research and biological experiment, that it has been found possible to obtain a pure and constant yeast.

By degrees, brewing has risen from a mere routine art to the rank of an important branch of technical chemistry. Our author places himself at the point of view indicated by Pasteur and Hansen and others. Here it must not be forgotten there is still abundant scope left for the ingenuity of the brewer.

The qualities of water and the determination of its

possible impurities are considered elaborately and fairly. The ammonia process, the permanganate method, and the tests of Heisch and Hansen are all described and criticised. The theory of previous sewage contamination is not accepted. The presence of sulphates in water is pronounced beneficial to the brewer. This view is quite in accordance with English practice, although in many Continental districts soft waters are preferred. Organic matter is, of course, pronounced as objectionable.

A very judicious caution is given in the chapter on planning a brewery. Says the author:—"Haylofts and oat-stores should on no account be anywhere near the fermenting-room, and it would be better if the prevalent winds did not blow from them towards the brewery. Hay teems with the spores of bacilli, and the light dust from corn is hardly less fertile, so that, if stores for them adjoin the fermenting-room, pure yeast is not to be expected."

Drains within the premises are also condemned. It is recommended that all waste waters and all matter capable of putrefaction should be carried out by means of deep wooden shoots.

This book will be found very useful, not merely to persons engaged in the fermentation trades, but to chemists who wish to place themselves in the brewer's point of view.

Treatise relative to the Testing of Water-wheels and Machinery; also of Inventions, Studies, and Experiments. With Suggestions from a Life's Experience. By JAMES EMERSON. Fourth Edition, 1892. Willimonssett: The Author.

THIS is one of the most singular books with which it has been our fate to come in contact. There are notices of improvements in the construction of turbines and other machinery. There are controversial passages anent rival inventors; there are denunciations of law and lawyers; of medicine and doctors; of colleges and their graduates; of over-education and its results; reports of trials or parts of trials in which the author shows an honest contempt for the system of examination and cross-examination; notes on marriage, divorce, and nudity, &c. There is literary criticism; the author stating that he would rather be the author of Pope's "Essay on Man" than of any other English work! There are contemptuous notices of Shakspeare and of Darwin. There are comments on Christianity and on the clergy of all denominations, which in former days would have been considered to verge unpleasantly close upon blasphemy.

Of course, any criticism of such a work in the CHEMICAL NEWS is out of the question.

CORRESPONDENCE.

THE LUMINOSITY OF FLAME.

To the Editor of the Chemical News.

SIR,—In your report of Professor Smithell's very interesting paper on "Experiments on Flame" and the discussion which followed, Sir George Stokes is said to have stated that "he understood from Professor E. Frankland that the latter had abandoned the view that luminosity was due to dense hydrocarbon vapours." In this, Sir George has misinterpreted my views on the subject.

In a lecture on coal-gas delivered at the Royal Institution in 1867, and published in the *Journal of Gas Lighting*, I said "I do not mean to assert that the decomposition of the hydrocarbons is never complete in the gas flame, and that under no circumstances does a single particle of elementary carbon ever separate in such a flame; but I do maintain that the luminosity in a gas flame is almost entirely due, not to this source, but to the ignition of the very dense vapours which are produced at the expense of

the gaseous hydrocarbons contained in the coal-gas." To this statement I still substantially adhere.

Although the classical researches of Heumann leave no doubt that solid or liquid particles do exist in gas and candle flames, my own subsequent experiments, a description of which I hope shortly to publish, go to show that such particles do not constitute the chief, or even an important, source of luminosity in these flames.—I am, &c.,

E. FRANKLAND.

The Yews, Reigate,
Sept. 17, 1892.

DISINTEGRATING ALLOY OF IRON, ALUMINIUM, AND MANGANESE.

To the Editor of the Chemical News.

SIR,—In Mr. T. W. Hogg's interesting "Note on some Alloys of Iron, Aluminium, and Manganese" (CHEMICAL NEWS, vol. lxxi., p. 140), his analysis of the disintegrating alloy accounts for only 94.29 per cent. "The deficiency," he says, "is no doubt due to oxygen, slight oxidation having taken place owing to the finely divided condition of the alloy." He evidently assumes oxidation to have been a consequence of disintegration, and not the cause thereof, as I imagine is the more likely. Were the disintegration due to some molecular change, then the fittest time for its accomplishment was when the alloy was at a red heat and its cohesive powers weakened. Whereas the twelve months required for its complete disintegration is more like the effect of slow atmospheric oxidation, hydration, or carbonation.

I have examined a few disintegrating compounds, and when air, moisture, and carbonic acid were excluded, these were quite permanent. Lime slag from manufacture of hematite iron often disintegrates or "falls," due to the hydration of CaO and oxidation of CaS contained in these slags. Firebricks that have been heated in contact with alkaline substance, and become saturated therewith, disintegrate into fine powder when exposed to the atmosphere.

Another instance I may cite is that of alkaline cokes perfectly stable at a red heat or when preserved dry, but crumbling slowly on exposure to weather.

In these cases I think it may be safely assumed that the substance acted upon by the atmosphere forms a minute network throughout the mass, and that the expansion of this on hydration, &c., is the cause of disintegration. In the alloy under consideration I can easily imagine an analogous action taking place, and the aluminium (although, it may be, forming some weak compound when molten) being thrown out when the mass cools, much in the same way as carbon is thrown out and forms a continuous network in ordinary pig-iron. However, it is to be hoped that Mr. Hogg will resume the investigation from this point of view, and publish his results in some future number, as it is rather a curious and interesting phenomenon.—I am, &c.,

GEORGE CRAIG.

Lugar Iron Works,
Gunnock, N.E.

Mining and Science Schools, Penzance.—Mr. H. Cavendish has been appointed Principal of the Penzance Mining and Science Schools in the place of Mr. H. Bailey. Mr. Cavendish is an Associate of the Royal School of Mines, where for three years he held a National Scholarship, and he also holds the honours certificates of the Science and Art Department in assaying, metallurgy, chemistry, principles of agriculture, &c. Mr. Cavendish has held the positions of Instructor of Assaying and Metallurgy at Onslow College, Chelsea, and of Demonstrator of Chemistry at Westminster Schools. He will now leave London to reside in Penzance, where he will commence work almost immediately.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 8, August 22, 1892.

Combustion-Heat of Various Chlorine Compounds.—MM. Berthelot and Matignon.

Glyoxylic or Dioxycetic Acid.—MM. Berthelot and Matignon.—These two thermo-chemical papers, whilst not admitting of useful abstraction, are not sufficiently important for insertion in full.

The Cholera: Its Causes and the Means of Preservation from It.—M. Pasteur, on presenting a recent work on this subject by Dr. Daremberg, called attention to the following points:—The author in one of the principal chapters of his book denounces emphatically the pollution of rivers by sewage, and equally the pollution of the soil by the distribution of sewage over the cultivated fields. He thinks that the germs of cholera, in the state of the exciting bacillus, may remain alive and virulent in the soil for several years, and may ultimately prove foci of cholera. The present cholera in the neighbourhood of Paris may be derived from the germs of cholera which have thus been preserved since the last epidemic of 1884. Dr. Daremberg, in the course of his work, cites experiments which have been recently made to protect domestic animals, and even man, from cholera.

Thermo-chemical Study of Certain Organic Bodies of Mixed Functions.—Leo Vignon.—The presence of the ketone group CO = distinctly annuls the basic functions in the base COR₂; the thioketonic group CS = allows these functions partially to subsist.

Determination of Peptone by Precipitation in the State of Mercury Peptonate.—L. A. Hallopeau.—The author's method is to precipitate the solution of peptone, free from other albumenoids, by a large excess of mercuric nitrate in a neutral or very slightly acid solution. The precipitate, which is white, flocculent, and voluminous, falls almost instantly to the bottom of the vessel. It is allowed to settle for eighteen to twenty-four hours until the supernatant liquid is limpid. The liquid and afterwards the precipitate are next poured upon a tared filter, which is washed with cold water until the washings are no longer precipitated by sulphuretted hydrogen. The increase of the weight of the filter, after desiccation at from 106° to 108°, represents the weight of the mercury peptonate; on multiplying this weight by the coefficient 0.666 we obtain that of the corresponding peptone. In order to determine this coefficient I precipitated with mercuric nitrate a known quantity of pure, dry peptone, prepared by the method of Henninger. I weighed the mercuric peptonate thus formed and calculated the proportion between the peptone used and the mercuric peptonate precipitated. I had previously ascertained by a combustion the purity of the peptone which served as an initial point. We may ascertain whether the precipitation with mercuric nitrate is complete by testing the filtrate for peptone by means of phosphomolybdic acid, which must not give a precipitate. The mercuric nitrate is purified from free nitric acid, which attacks the peptonate, by the following method:—100 or 150 grms. of pure mercuric nitrate are heated on the water-bath for fifteen to twenty minutes with 1 litre of water. The filtrate is heated almost to ebullition in a porcelain capsule. At this moment we add, whilst stirring, a few drops of solution of sodium carbonate until the precipitate of mercuric oxide formed ceases to re-dissolve. The liquid is filtered and diluted to 1 litre. The presence of chlorides does not interfere if a large excess of mercuric nitrate is used.

If the liquid in question contains other albumenoids they must be previously eliminated by the following process:—The liquid, if acid, is exactly neutralised with sodium carbonate when syntonine is precipitated. It is collected on a tared filter and washed with cold water. The increase of the weight of the filter (dried at 105°) shows the weight of syntonine. To the filtrate is added a drop of acetic acid, and it is heated for thirty minutes on the water-bath. Albumen is precipitated in flocks, which are collected on a tared filter and determined in the ordinary manner. To the filtrate we add nitric acid, drop by drop, until a turbidity is formed. The liquid is stirred for an instant, and the precipitate (hemi-albuminose) is allowed to settle. It is thrown upon a filter and washed with a little water containing a trace of nitric acid.

Zeitschrift für Analytische Chemie.
Vol. xxx., Part 6.

New Exsiccator.—W. Hempel places the hygroscopic agent (calcium chloride or sulphuric acid, &c.) above the substance to be dried. E. Biltz calls in question the utility of this arrangement, and W. Hempel replies.

An Extraction Apparatus.—M. Karaz (*Zeit. Angew. Chemie*).—The principle of this device is essentially well known.

Cylinders with Overflow-Vessels.—R. Frühling and Jul. Schulz (*Zeit. Angew. Chemie*).—To prevent an overflow from cylinders used in taking the specific gravity of fluids by means of a hydrometer, the authors propose a concentric vessel surrounding the upper part of the cylinder.

New Determinations of the Specific Gravities of Hydrochloric Acids at Different Concentrations.—G. Lunge and L. Marchlewski (*Zeit. Angew. Chemie*).—A very complete set of tables.

Volumetric Determination of Tellurium.—B. Brauner.—This paper will be inserted in full.

Volumetric Determination of Sulphates.—H. Quantin.—From the *Bull. Soc. Chim. de Paris*.

Detection and Determination of Nitrous Acid.—P. F. Frankland.—From the *Journ. Chem. Soc.*

Detection of Alcohol in Varnishes, Pharmaceutical Preparations, &c.—Ad. Tscheppe (*Pharm. Rundschau and Chem. Zeit.*).—The author puts in a test-glass concentrated nitric acid (70 per cent), and pours above it the liquid in question. In presence of alcohol there appears a greenish colour, which in a few minutes passes into a brilliant deep emerald. Gradually there takes place a faint evolution of gas, and the characteristic odour of ethyl nitrite is recognised.

Detection of Cinnamic Acid.—T. L. Phipson.—From the *CHEMICAL NEWS*.

Detection of Resorcin.—L. Reuter (*Pharm. Zeit. and Chem. Zeit.*).—Already inserted.

Recognition of Furfural.—E. Nickel (*Chem. Zeit.*).—Already inserted.

The Kjeldahl Process.—A. Atterberg (*Chem. Zeit.*).—The author has re-examined Gunning's modification of the original method, and finds that it yields correct results with such substances as the alkaloids, the azo-compounds, &c.

Determination of Glycerin.—J. Alfred Wanklyn and W. Johnstone.—From the *CHEMICAL NEWS*.

Rose's Method for the Determination of Alcohol.—Rud. Benedikt, also Leo Grünhut (*Chem. Zeit.*).—Both authors find the method untrustworthy.

Examination of the Sizing of Paper.—O. Schluttig and G. S. Neumann (*Papier Zeit.*).—The author founds his method on the permeability of the paper for solution of ferric chloride, applied upon one side of the sheet to be tested and solution of tannin applied on the other.

Detection of Naphthaline, α - and β -Naphthol.—L. Reuter (*Pharm. Zeit.* and *Chem. Zeit.*).—The author to discriminate between these three substances utilises the colour reactions which they give if heated for ten minutes with melted chloral hydrate. The colour reactions vary according as we use chloral hydrate alone, or, in addition, five drops of hydrochloric acid, or hydrochloric acid with zinc. The reactions are as follows:—

	0.1 grm. naphthalin.	0.1 grm. α -naphthol.	0.1 grm. β -naphthol.
With 2.5 grm. chloral hydrate.	Intense less.	Intense transparent, non-fluorescent.	Pure blue, transparent, non-fluorescent.
With 2.5 grm. chloral hydrate + HCl.	Almost colourless, faint rose.	Intense greenish blue, opaque.	Deep Intense yellow, transparent.
With chloral hydrate as before, + zinc.	Violet.	Deep violet-blue, on adding water violet flocks which dissolve in alcohol with a reddish violet fluorescence.	Deep dark brown; on adding water separation of a smeary substance which dissolves in alcohol with a yellow colour, with blue fluorescence.

Methods Proposed for determining Paratoluidine in Commercial Toluidines.—F. F. Raabe (*Chem. Zeit.*).—Already inserted.

Analysis of Milk.—A collection of extracts from a variety of journals for which we must refer to the original.

Recognition of Linen Fibre and its Distinction from Cotton Fibre.—M. Wiesner (*Dingler*).—The author applies chromic acid. Linen fibre after a few seconds appears as if cut up into transverse portions, whilst cotton fibre, if similarly treated, is split up as if into bristles.

Conditions of Calcium Carbonate in the Soil.—F. Reverdin and Ch. de la Harpe (*Chem. Zeit.*) propose a method for determining the assimilable lime in the soil. The method depends on the consideration that oxalic acid and the oxalates only attack the surfaces of the particles of calcium carbonate and convert them into calcium oxalate, whilst only these same surfaces are capable of assimilation by vegetation.

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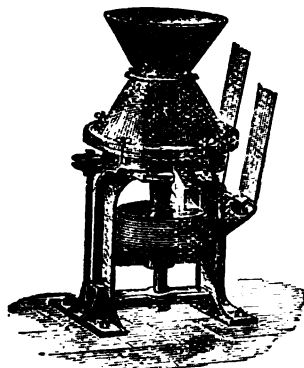
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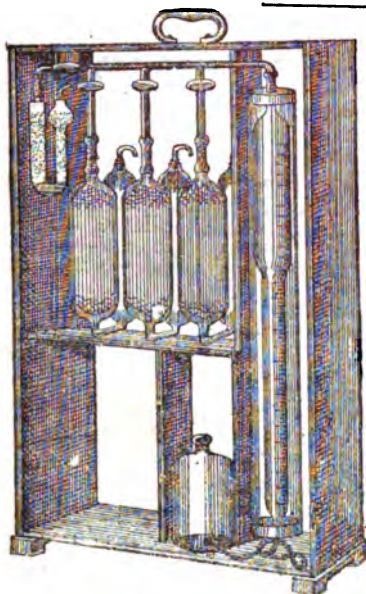
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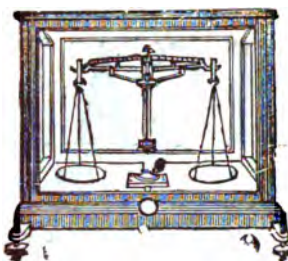
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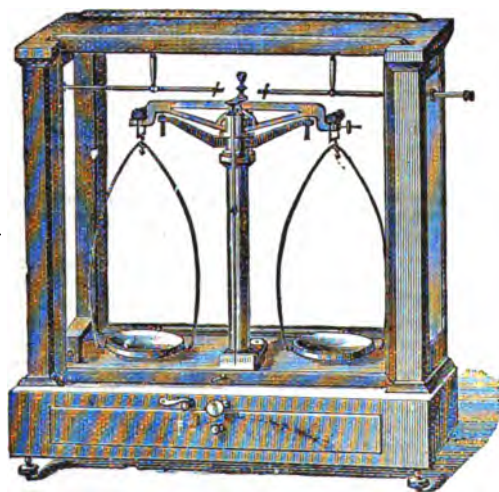


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THE COLOURS AND ABSORPTION-SPECTRA OF THIN METALLIC FILMS AND OF INCANDESCENT VAPOURS OF THE METALS; WITH SOME OBSERVATIONS ON ELECTRICAL VOLATILITY.*

By WILLIAM L. DUDLEY.

SEVERAL years ago the writer began to investigate methods for obtaining metals in thin films, with a view to the study of the relations existing between their colour by transmitted light and that emitted by their incandescent vapours; also to the study of their absorption-spectra. A number of methods were resorted to; for instance:—

1. Volatilisation by boiling and condensation on glass;
2. Electro-deposition and removal of the "base" on which the metal is deposited by a suitable solvent;
3. Reduction of a salt which had been spread in a thin and uniform layer on the surface of a transparent base;
4. Volatilisation by the electric arc between terminals of the metal enclosed in a glass tube filled with an inert atmosphere; and
5. Volatilisation by the condensed electric spark under similar conditions.

Each method had its value in particular cases, but no one method seemed to be capable of universal application, although the last mentioned was generally applicable. I will describe briefly the various methods employed.

(1) Volatilisation by boiling was resorted to in dealing with potassium, sodium, and lithium. Potassium, which had been freed from all mechanical impurities and hydrocarbons, was introduced into a glass tube filled with an atmosphere of hydrogen or nitrogen which was highly attenuated by a pump, and sealed. The portion of the tube in which lay the globule of metal was gradually heated over a Bunsen burner until the potassium boiled, when the tube was immediately withdrawn from the flame. The vapour of the potassium condensed in a thin film on the cooler portions of the tube, and exhibited in the thinnest parts colours by transmitted light ranging from violet to blue as the thickness increased, while by reflected light the film had the usual silvery metallic lustre of potassium. The film is not permanent. The brilliant colours gradually fade, until after some days they have completely disappeared, owing to the thin layer slowly drawing itself together into minute globules which to the unaided eye give to the whole surface a frosted appearance. By again heating the metal to boiling as before a new film can be produced.

Sodium and lithium were treated in the same manner as potassium. Sodium, however, gave a yellow-brown film, which was due to its action on the glass; the colour was at first ascribed to the reduction of silica, but when lithium was treated in the same way the glass was also attacked, the colour of the film being deep red-brown. The glass was permanently coloured in each case, the metals having combined chemically with it, as one would naturally expect. The colour conveyed by each was, however, a source of surprise, since it approached more or less closely, even under these circumstances, to that of its incandescent vapour. It may be accounted for in the same way as is gold "ruby" glass, i.e., is due to the presence of finely divided metal distributed through the glass. If thin gold leaf, which exhibits a fine green colour by transmitted light, be spread out on a sheet of glass and heated to 316° or over, the colour becomes red,

and if the temperature has not been so high as to incorporate the gold with the glass, the green colour may be restored by simply burnishing the surface (Faraday, *Phil. Trans.*, 1857, 145; also his "Experimental Researches in Chemistry and Physics"). The ruby colour of the glass is held to be due to the gold in a finely divided state, and the colours given to glass by sodium and lithium may be due to the same cause. Many kinds of glass were employed,—all, of course, without lead in their composition,—and the effect was always the same.

(2) Electro-deposition is of limited application; gold films may, however, be readily produced, owing to the ease with which this metal is deposited; its resistance, too, to the action of acids making the separation of the film from the metal upon which it is deposited a simple matter (Outerbridge, Paper by Eggleston, *Trans. Am. Inst. Min. Eng.*, vii., p. 91). A difficulty is encountered in this method in efforts to obtain films of proper thickness; this is, however, largely obviated by a method employed by Kundt ("Ueber die Brechungsexponenten der Metalle," *Ann. der Phys. Wied.*, xxxiv., 469), in which he obtains a wedge-shaped film by placing the cathode horizontal in the bath and the anode very near, and perpendicular to, the surface of the cathode. Thus the film tapers out in a very thin edge. Arsenic deposited on glass by decomposing arsine may prove a good surface upon which to make the deposits, as it could easily be dissolved off of the film by sodium hypochlorite or some other suitable solvent. I have never tried it, however, as I found that other methods served my purpose in most instances.

(3) The reduction of a thin film of the metallic salt was found unsatisfactory for various reasons, and was not employed, although films of platinum could be obtained quite easily, giving a purple colour by transmitted light.

(4) The electric arc between terminals of the metal to be volatilised proved successful in a few cases. The terminals were inserted into a glass tube filled with an inert atmosphere, and brought in contact for an instant. The metal was suddenly vapourised and thrown upon the glass, but was usually granular or powdery, of a black or brown colour, altogether unsatisfactory, owing to its discontinuous character.

(5) The condensed spark between two points of the metal enclosed in a glass tube, exhausted, or filled with an inert atmosphere highly attenuated, serves well in many cases. For descriptions of this method in detail I refer to papers by Wright ("On the Production of Transparent Films by the Electrical Discharge in Exhausted Tubes," *Amer. Journ. Sci.*, [3], xiii., 49; xiv., 169), Hartley ("On Films produced by Vapourised Metals and their Applications to Chemical Analysis," *Proc. Royal Society*, xlv., 88), and Crookes ("On Electrical Evaporation," *CHEMICAL NEWS*, lxiii., 287). Hartley, however, volatilised the metals in the air, and consequently only a few of the films were metallic. The facility with which metals volatilise by this method varies very much, those of low atomic weights showing, as a rule, more resistance than the heavier metals to the action of the spark. According to Crookes, this power of resistance does not increase regularly as the atomic weight decreases. No relationship has yet been discovered between the degree of electrical volatility and any known constant. Some relationship might be discovered if the volatilisation were carried on under such conditions of temperature and pressure as would most likely insure similar molecular conditions in each case. This might possibly involve the melting-point, as well as the atomic weight, as a factor.

If the order of the electrical volatility of the metals as found by Crookes be compared with Lothar Meyer's curve of atomic volumes, it will be found that the volatile metals lie at or near the minima of the curves, close together on the ascending sides in the periods IV., V., and VII., alternating from one to the other. Magnesium and aluminium, which are practically non-volatile, lie on the

* From the *American Chemical Journal*, vol. xiv., No. 3.

Metal.	Colour of Film.	Observer.	Colour of Incand. Vapour.	Observer.	Colour of Incand. Vapour as indicated by spectrum.
Gold	{ Pinkish, violet, blue, blue-green.	Faraday, Wright, and others.			
Heated to 316° ..	Green.	Crookes and others.	Green.	Dudley	Green.
Heated on glass	{ Red.	Faraday and Wright.			
Silver	Deep blue.	Wright.	{ Blue.	Stas.	
			Yellow-green in electric arc.	Dudley.	Yellow-green.
Copper	Green.	Wright, Fleming.	Green.	Dudley.	Green.
Aluminium	{ Fine blue.	Fleming.	Green-blue.	Dudley.	Green-blue.
	Brownish.	Wright.			
Bismuth	Grey-blue.	Wright.	Blue, slightly greenish.	Dudley.	Blue-green.
Platinum	{ Blue-grey.	Wright.	Blue (?)	Dudley.	Blue.
	Purple.	Dudley.			
Palladium	Smoky brown.	Wright.	Green.	Deville and Debray (?)	Green.
Lead	{ Smoky brown, inclining toward olive.	Wright.	Blue.	Dudley.	Blue.
Zinc	{ Grey blue, less deep than Ag, deeper than Bi.	Wright.	Green-blue.	Dudley.	Green-blue,
Cadmium	{ Grey blue, about same as Zn, slightly less intense.	Wright.	Green.	Dudley.	Green.
Magnesium	{ Grey blue, similar to Zn and Cd, but less clear.	Wright.	Green.	Wright.	Green.
Tin	Brown-grey.	Wright.	Blue (?)	Dudley.	Blue-green (?)
Iron	{ Neutral tint with faint tinge of brown.	Wright.	Green-blue.	Dudley.	Green-blue.
Nickel	Grey or brown-grey.	Wright.	Blue-green.	Dudley.	Blue-green.
Cobalt	Grey or brown-grey.	Wright.	Green-blue.	Dudley.	Green-blue.
Tellurium	Dull purple.	Wright.	Golden yellow.	Gernez.	Orange-yellow.
Potassium	Blue-violet.	Dudley.	Violet.	Davy.	Violet,
Sodium heated on glass	Brown-yellow.	Dudley.	Yellow.	Davy.	Yellow.
Lithium heated on glass	Dark brown red.	Dudley.	Red.	Arfvedson (?)	Red.

descending side of period III. Aluminium, which is less difficult to volatilise than magnesium, is nearer the minimum of the curve. The metals given in the order of their electrical volatility alternate in the periods as follows:—

Metal,	Comparative electrical volatility.—Crookes.	Period.
Pd	108°	V.
Au	100°	VII.
Ag	82° 68	V.
Pb	75° 04	VII.
Sn	56° 96	V.
Pt	44° 00	VII.
Cu	40° 24	IV.
Cd	31° 99	V.
Ni	10° 99	IV.
Ir	10° 49	VII.
Fe	5° 50	IV.

A thin, reguline, and coherent film of a metal transmits light of a colour remarkably similar to that emitted by its incandescent vapour. The colour of the vapour of a metal varies with the temperature. Just above its boiling-point the vapour of sodium is purple; at incandescence, yellow. The vapour of potassium is green; at incandescence, violet. Silver in distilling gives off a blue-white vapour, while that volatilised by the electric arc passing between silver electrodes emits yellowish-green light. The colour of the film obtained in many cases agrees very well with that of the incandescent vapour. In some instances, however, there is no similarity (see table above), a fact which is probably due to failure to obtain the proper conditions for the volatilisation and deposition. The perfection and continuity of the deposit is easily destroyed by very slight changes in the conditions. For instance, the aluminium film deposited by Wright by condensed sparks was brownish,

while that observed by Fleming (Discourse delivered at the Royal Institution, *The Electrician*, xxiv., 393), which resulted from the volatilisation of an aluminium connection in an overheated incandescent lamp, was of a "fine blue" colour in the thinnest portions.

The colour of the incandescent vapour of a metal is the resultant of the colours of the various rays emitted, and depends on the number and intensities of these rays; the colour can therefore be fairly predicted on examining a table of the wave-lengths and relative intensities of the spectral lines of the metal.

I give above a table containing a number of metals, in which is given the colour of the films by transmitted light, and the colour of the incandescent vapour as observed and as indicated from the spectral lines. The authorities are given as far as possible. In some cases I have been unable to find any mention of the colour of the incandescent vapour, although I am sure it must have been observed. In such cases I put my own name.

The colour of a film will vary somewhat with the thickness, but as far as I have observed the colours extend over a very limited portion of the spectrum. Each metal possesses a strong tendency toward a characteristic colour which is produced when the film is as thick as it can be to transmit any light.

Absorption-Spectra of Metallic Films.

Many of the films which corresponded closely in colour to the incandescent vapour of the respective metals were examined carefully as to their absorption spectra by throwing a powerful beam of white light through them. If the same molecular condition existed in the film as in the incandescent vapour we would expect to have the same absorption. In other words, the dark lines of the absorption spectrum of the film should coincide with the bright lines of the emission spectrum of the incandescent

vapour. I found in every case, however, that the films gave simply general absorption, no bands or lines being indicated.

THE SYNTHESIS OF SUGARS.

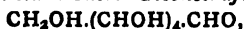
By W. E. STONE, Purdue University.

DURING the last five years there have appeared in the *Berichte der Deutschen Chemischen Gesellschaft* a series of remarkable papers presenting the details of the researches of Emil Fischer and his associates upon the synthetical production of sugars. These researches are of great theoretical interest from the light they cast upon the constitution of the sugars, as well as from the many new and important reactions which they have developed. As a whole this work may be classed among the notable achievements of the decade in organic chemistry. Aside from this, so much has been contributed to the stock of positive knowledge about this important group of compounds, that the results are of equal interest to the student of either theoretical or applied chemistry. In reviewing the work one cannot escape the impression that it is the beginning of many important results, both theoretical and practical, and that future research with these bodies must be largely prosecuted along the lines here laid down.

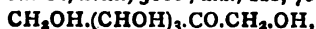
On account of the interrupted appearance of these papers it is thought that a comprehensive *resumé* of the same will bring the results into more accessible form, especially for those who do not read German with facility.*

To produce sugar synthetically has been one of the air castles of organic chemistry since the possibility of organic synthesis was established. Two great obstacles, however, have prevented the successful ending of many, more or less scientific, experiments in this direction. These were, first, ignorance of the chemical constitution of the sugars as explained by modern chemical theory; and second, the absence of successful methods for the separation and recognition of small quantities of sugars, especially in the presence of a large proportion of impurities, as well as of synthetical methods suited to the complex and unstable sugar molecule. Finally, the results obtained after these obstacles were overcome can only be understood and explained by the principles of the modern theories of chemistry, which ascribe to each chemical molecule a distinct geometrical structure, and explain the phenomena of isomerism upon the basis of the different geometrical arrangement of the atoms composing the molecule.

So late as 1886 the only sugars of the glucose or hexatomic group ($C_6H_{12}O_6$) which had been well studied and specifically characterised were *dextrose*, *levulose*, and *galactose*. As these represented the derivatives of other more complex sugars (sucrose, maltose, lactose, &c.), they stood as a fairly well-defined nucleus about which were clustered numerous other, more or less thoroughly studied, compounds. Of these sugars, dextrose and galactose had been shown to be normal pentoxy-aldehyds (*Berichte d. Deutschen Chem. Gesellschaft*, xxiii. 2115),—



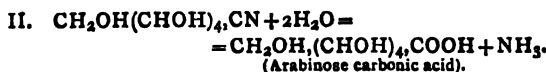
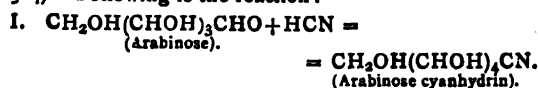
while levulose was regarded as a normal pentoxy-ketone (*Berichte D. Ch. G.*, xviii., 3066; xix., 221, 767, 1916),—



all three being regarded as theoretical derivatives of the normal hexatomic alcohol, $C_6H_{14}O_6$. These conclusions were arrived at from the behaviour of the given sugars toward oxidising and reducing agents. Another body, for many years classified with the glucose group, viz.,

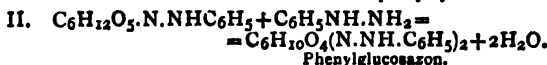
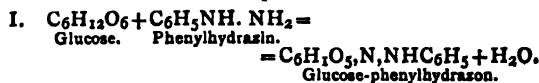
arabinose, was found in 1887 to be a normal tetroxy-aldehyd, $CH_2OH.(CHOH)_3.CHO$, corresponding to the pentatomic alcohol, $C_5H_{12}O_5$ (*Berichte D. Ch. G.*, xx., 339). Definite knowledge of the constitution of these four sugars was the first important step toward their synthesis, showing as it did their relation to other carbon compounds. But this theoretical knowledge alone would never have sufficed to accomplish even the beginning of the extraordinary syntheses which are to be credited to Fischer. They were only possible by the aid of certain reactions and methods, most of which have also originated with the same investigator.

The first of these reactions, however, we owe to H. Kiliani, who showed that hydrocyanic acid could be added to an aldehyd or ketone sugar, forming a cyanhydrin, which on being heated with a basic oxide (baryta) becomes saponified, producing a monobasic oxy-acid with one more carbon atoms than the sugar employed (*Berichte D. Ch. G.* xviii., 3066; xix., 221, 767, 1128, 1914). Following is the reaction:—



This typical reaction is the same by which Kiliani proved the constitution of arabinose, and has since been made of use of by Fischer for the synthetical step from a lower to a higher group of sugars, as for instance from $C_6H_{12}O_6$ to $C_7H_{14}O_7$.

A more general reaction than this is that discovered by Fischer between aldehyds or ketones and phenylhydrazin (*Berichte D. Ch. G.*, xvii., 572), and first applied by him for the characterisation of sugars (*Berichte D. Ch. G.*, xvii., 579). The reaction occurs readily with all aldehyd or ketone sugars forming characteristic crystalline, insoluble compounds. The method is as follows:—A 10 per cent watery solution of the sugar receives an acetic acid solution of phenylhydrazin, and, on heating the mixture in a water-bath at 75° to 85°, there soon begins a precipitation of fine yellow crystals of the composition $C_{18}H_{22}N_4O_4$ (if the sugar be of the $C_6H_{12}O_6$ group). The reaction occurs in two phases as follows:—



The first product is, in nearly all cases, soluble in water, but, on heating, the "osazon," containing a second molecule of phenylhydrazin, is precipitated. The "osazon" thus produced from all of the sugars which reduce Fehling's solution are stable bodies, easily separated from accompanying impurities, easily purified and serving to characterise—either by analysis or melting-point—the sugars from which they are derived. The melting-points of the "osazons" of the well-known sugars illustrate this:—

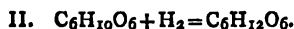
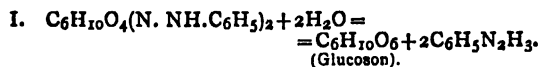
Glucosazon, 205°	Maltosazon, 206°
Galactosazon, 193°	Rhamnosazon, 180°
Sorbinosazon, 164°	Arabinosazon, 560°
Lactosazon, 200°	Xylosazon, 160°.

This reaction is safely the most important means yet discovered for separating and identifying small quantities of sugars in the presence of impurities or foreign bodies.

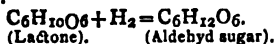
Fischer has also succeeded in regaining the sugar from its osazon, and the latter has thus served in several cases as a means for isolating a newly prepared sugar, yielding

* Fischer himself has reviewed a portion of this work before the German Chemical Society, in June, 1890. See *Berichte*, xxiii., 2114. The work previous to 1890 has also been reviewed by Dr. E. H. Keiser in *American Chemical Journal*, xi., p. 277; and xii., p. 357.

it up again in a pure form. This result is obtained by treating the osazon with fuming hydrochloric acid, by which the phenylhydrazin is split off, leaving a body called an "oson," which by reduction becomes the sugar (*Berichte D. Ch. G.*, xxii., 87). Following is the reaction:—



A third reaction, which has played a very important part in these syntheses is the method devised by Fischer for the reduction of the acids of the sugar group to their corresponding aldehyds (*Berichte D. Ch. G.*, xxii., 2204). This reaction does not occur with the free acids; but Kiliani has shown that the oxy-acids of the sugar series easily form lactones by loss of water, on evaporation of their watery solutions. Such lactones were found by Fischer to be readily reduced to corresponding aldehyds (sugars) by the action of sodium amalgam upon their watery solution.



This reaction occurs, however, only in an acid solution, i. e., when small quantities of sulphuric acid are added successively to the solutions in which the reduction is taking place.

It will be seen that this reaction, in connection with the addition of hydrocyanic acid to an aldehyd sugar, as already described, supplies all the steps for the synthesis of one sugar from another containing one less carbon atom, the compounds being derived from each other in this order:—Arabinose ($\text{C}_5\text{H}_{10}\text{O}_5$), arabinose-cyanhydrin, arabinose-carbonic acid, the lactone of this acid, and finally the glucose with six carbon atoms ($\text{C}_6\text{H}_{12}\text{O}_6$).

Several other new reactions, of quite equal importance to the success of these researches will be described later, but these suffice to introduce the work of Fischer and his collaborators.

It having been established that the glucoses possessed the structure of aldehyds or ketones, there naturally followed attempts to produce the same by a mild oxidation of the corresponding hexatomic alcohols. All the earlier attempts to carry out this reaction led, however, to no definite results, although the products thus obtained from mannitol and dulcitol exhibited some of the properties of the sugars (fermentability and reducing action upon Fehling's solution). Fischer repeated this oxidation, and, by means of the phenylhydrazin, isolated the sugar thus obtained, found that it had the same structure as grape sugar (a pentoxo-aldehyd), and ascertained that the latter was not the true aldehyd of mannitol, as had been supposed, but that it belonged to a different series of stereoisomeric compounds (*Berichte D. Ch. G.*, xxii., 374). The sugar obtained from mannitol was called mannose, and has since been obtained by hydrolysis from various natural materials (Tollens and Gans, *Annalen Chem. u. Pharm.*, cclxvi., 256; Reiss, *Berichte*, xxii., 609, 3218).

In a similar manner has been obtained from the tetraatomic alcohol erythrit a sugar called erythrose, and from the triatomic alcohol glycerin a sugar named glycerose (*Berichte D. Ch. G.*, xxii., 1088).

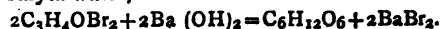
All this was far removed from the actual synthesis of sugars, and the experimenter was at this time far from seeing his way through the different steps, now so well defined.

The way to the actual building up of the sugar molecule had been suggested by different workers before Fischer finally succeeded. Butlerow's methylenitan (*Annalen Chem. u. Pharm.*, cxx., 295), obtained from formaldehyd, a sweet, reducing, but not fermentable and optically inactive syrup, is regarded by Fischer as the beginning of this matter; and indeed this was used by Baeyer as the basis of his theory for the formation of

sugar in the plant, viz., the polymerisation of formaldehyd. Later, Tollens made a similar observation, upon treating formaldehyd with lime-water;* and, following him, Loew studied the product to which was given the name *formose* (*Fourn. Prakt. Chemis* [2], xxxiii., 321).

In none of these cases was the product well characterised or isolated. In Fischer's hands, however, the formaldehyd derivative was shown to be a mixture of various sugar-like bodies, of which one—non-fermentable and optically inactive—still retains the name *formose* (*Berichte D. Ch. G.*, xxi., 989).

Meantime came a most important discovery by Fischer (*Berichte D. Ch. G.*, xx., 1093, 2566), viz., that a sugar-like body was produced by treating acrolein bibromide with baryta-water,—



From the products of this reaction were isolated by means of phenylhydrazin two isomeric sugar-like bodies called respectively α - and β -acrose.

Identical with the above were products obtained by treating glycerose with a weak alkali (*Berichte D. Ch. G.*, xx., 3384). This latter attainment is of physiological interest because secured under mild conditions, possible in living organisms.

Of these synthetic products the α -acrose was the most important. This was now found to be identical with one of the bodies resulting in small quantities along with formose, from the polymerisation of formaldehyd (*loc. cit.*). This α -acrose was separated from other reaction products by means of phenylhydrazin as the α -acrosazon, which, by the method already referred to, yielded α -acrosone, and this again, by reduction, a sweet syrup which reduced Fehling's solution, fermented with yeast, yielded levulinic acid on treatment with hydrochloric acid, and, in short, gave all the reaction of the glucoses, but was *optically inactive*. By means of sodium amalgam it was reduced to a hexatomic alcohol (α -acrit), which closely resembled mannitol, save that it was also *optically inactive* (*Berichte D. Ch. G.*, xxii., 97). This optical property was at that time impossible to explain, but has since been found to characterise an altogether new and numerous series of synthetic sugars.

The α -acrose was regarded as a true sugar, and being derived from formaldehyd (or glycerose) as described, the synthesis of a member of the sugar group may be regarded as complete at this stage, although there still remained a gap between the artificial sugar and any natural one. To accomplish so much, however, had required great patience and skill, involving the treatment of large amounts of materials, while the ultimate products were obtained in such small quantities as to preclude their close study. The synthesis of sugars would never have reached anything like its present stage if dependent on the operations thus far described.

(To be continued.)

PIPETTES FOR MEASURING POISONOUS LIQUIDS.

By ALEX. F. REID, of Bonshaw, Stewarton, N.B.

In my last contribution (*CHEMICAL NEWS*, lxx., p. 125) I described some improvements upon burettes. I will now describe two improved pipettes for measuring the poisonous liquids.

In measuring poisonous liquids with a pipette it is usual to put a piece of cotton-wool or other like material, moistened with an antidote, in the top of the tube of the

* *Berichte D. Ch. G.*, xv., 1629. Since this, Tollens and Wiegand have shown that a mixture of formaldehyd and acetaldehyd with lime-water, on standing three to four months, polymerised to form penta-erythrit, $\text{C}(\text{CH}_2\text{OH})_5$. *Annalen Chem. u. Pharm.*, cclxv., 316.

Pipette. In the pipettes I am going to describe this Precaution is obviated.

Fig. 1 is a common pipette with about 6 inches of india-rubber tube attached to the upper end of it. To this india-rubber tube is attached an india-rubber ball by means of a short piece of glass tube. This india-rubber ball has a hole in its side. To fill the pipette with liquid the moistened thumb of the right hand is placed upon the orifice of the ball, and the latter compressed. The point of the pipette is now put into the liquid, and the ball slowly allowed to regain its normal dimensions, still keeping the thumb on the hole. The liquid rises in the pipette, and when it comes to the mark the india-rubber tube is clipped by the thumb and finger of the other hand. The thumb is now taken away from the hole in the ball,

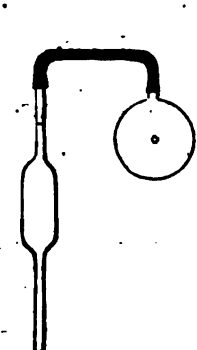


FIG. 1.



FIG. 2.

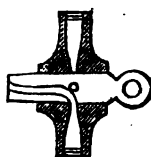


FIG. 3.

then the thumb and finger from the india-rubber tube, and the liquid allowed to run out. After some practice this can be done as easily as—in fact more easily than—with the mouth, as you can more readily see what you are doing.

Fig. 2 is a form of pipette in which the india-rubber ball may be attached directly to the top of the pipette, and in which it is not necessary to always fill the pipette to the same mark, a three-way stopcock being in the place where the mark would otherwise be. The liquid is drawn up by the compressed ball into the upper part of the tube, and the stopcock slightly turned. By turning it further, into the position shown in Fig. 3, the measured liquid runs out of the pipette.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1892.

By WILLIAM CROOKES, F.R.S.,

and

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, *Metropolis Water Act, 1871.*

London, September 12th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from August 2nd to August 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and

Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

As will be seen from the Tables, the water-supply to the Metropolis during the month of August continued to be of excellent quality, the proportions of organic matter present, estimated alike by the combustion and oxygen processes, and by the degree of colour-tint, being, as now for some months past, extremely small. In the case of the Thames-derived supplies, for example, the mean proportion of organic carbon amounted to 0.115 part in 100,000 parts of the water, this being 0.002 part in excess of the mean for June, and 0.020 part in excess of the mean for July, minute differences of no practical significance. The maximum proportion of organic matter present in any single sample examined was found to be identical with that of the previous month, or 0.152 part in 100,000 parts, corresponding roughly to about a quarter of a grain of organic matter per gallon. The amount of organic matter found in the water furnished by the Chelsea Company was again exceptionally low, the mean proportion of organic carbon in that Company's supply and in the supply of the New River Company, or 0.078 and 0.079 part in 100,000 respectively, being to all intents identical.

From time to time, in periods of flood or after violent rainfall, we find in the course of our examinations of the daily supply furnished by the different companies, an occasional sample which, when viewed in bulk, exhibits a distinct turbidity; and from some cause or another, one such instance was met with among the 175 samples examined last month. More often, but still only occasionally, samples are met with manifesting on careful examination through a depth of two feet, a slight deficiency in brightness. These samples we have been accustomed all along to indicate by the letters V.S.T., standing for "very slightly turbid," an expression, however, suggesting somewhat more than is warranted, since under common observation these samples would be regarded as perfectly clear.

The effect of any ordinary excess of rainfall is, as doubtless with an increase of storage capacity that of an extraordinary excess would be, almost inappreciable. During the past month the rainfall at Oxford was 1.38 inch above the average; and of the entire 3.62 inches of fall, 1.02 inch was contributed on a single day, and over half an inch on each of two other days with only one intervening day between them. Yet in the entire month's supply furnished by three out of the five Thames Companies, not a single sample having even to be indicated by the letters V.S.T. was met with.

We are, Sir,

Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.

CHEMICAL EXAMINATION OF HAND-WRITING.

By A. ROBERTSON and J. HOFMANN.

THE authors draw lines across the letters or figures with quill pens dipped in the following reagents, and observe the changes where the ink and the reagent meet, using, if needful, a magnifying power of 100 diameters. The reagents are:—(1) A 3 per cent solution of oxalic acid; (2) a 10 per cent solution of tartaric acid; (3) a 2 per cent solution of chloride of lime; (4) solution of 1 part stannous chloride in 1 part hydrochloric acid and 10 parts

		Logwood with—				
Reagents.	Iron and gall ink.	Potassium chromate.	Copper sulphate.	Nigrosine.	Vanadium ink.	Resorcin ink.
Oxalic acid	Disappears.	Violet.	Orange.	No change.	Turns pale and runs a little.	Bright red.
Citric acid	Turns pale.	Violet.	Orange.	Runs dark blue.	Turns pale and runs.	Disappears.
HCl.. .. .	Disappears, but leaves a yellow.	Purple red.	Blood red.	Little change.	Slightly paler and runs slightly.	Light rose.
Sulphuric acid ..	Disappears.	Red.	Purple red.	No change.	Slightly paler.	Bright red.
Nitric acid	Disappears.	Red.	Purple red.	Runs slightly.	Slightly paler.	Light rose.
Stannous chloride..	Disappears.	Red.	Magenta.	No change.	Slightly paler.	Disappears.
Sulphurous acid ..	Turns pale.	Violet grey.	Red.	No change.	Slightly paler and runs.	Turns paler.
Gold chloride.. ..	Slightly paler.	Red-brown.	Brown.	No change.	No change.	Runs brown.
Sodiumthiosulphate and NH ₃	Dark red.	Nochange.	Dark blue.	Dark violet, runs.	Runs much.	Brown.
Ferrocyanide and HCl	Blue.	Red.	Brick-red.	No change.	No change.	Rose.
Sodium hydroxide..	Dark red.	Brown.	Dark red, runs.	Dark violet, runs.	Dirty brown, runs.	No change.
Chloride of lime ..	Disappears.	Disappears.	Disappears leaving a yellow stain.	Brown.	No change.	Brown.

of water; (5) sulphuric acid at 15 per cent; (6) hydrochloric acid at 10 per cent; (7) nitric acid at 20 per cent; (8) saturated solution of sulphur dioxide; (9) 4 per cent solution of gold chloride; (10) solution of 1 part potassium ferrocyanide in 1 part hydrochloric acid and 10 parts water; (11) solution of 1 part sodium thiosulphate (hyposulphite) in 1 part ammonia and 10 parts water; (12) 4 per cent soda-lye.

The subjoined Table shows the results. The results with tartaric acid are not tabulated.—*Chemiker Zeitung*.

THE INFLUENCE OF THE CARBOXYL GROUP ON THE POISONOUS ACTION OF THE AROMATIC COMPOUNDS.

By W. NENCKI and H. BAUTMY.

THE researches of the authors are intended to show, on the basis of earlier as well as recent facts, that the introduction of the carboxyl group, CO₂H, into the molecule of a great number of aromatic compounds involves a great decrease of their toxic action.

As the main cause of poisoning is to be sought in reductive phenomena, the diminution of the toxic action may be explained by the consideration that it represents a group saturated with oxygen which is not further reduced in the organism. Benzon, naphthaline, pyridine, quinoline, are well known to be rather powerful poisons. Benzol- and naphthaline carbonic acids are feeble poisons, and such will be found to be the corresponding carboxyl-compounds of quinoline and pyridine. Whilst the phenols exert a powerfully toxic action this is considerably lessened in the corresponding carbon acids. Carboxyl, however, diminishes the toxic power not only in the aromatic hydrocarbons, amines, and phenols, but also in very complex aromatic compounds. Antifibrine (?) is eliminated in the urine as orthoxycarbonil, the sulpho-salt of which possesses, according to Demme, a considerably poisonous action. The corresponding orthoxyl-carbonil-carbonic acid,—a white crystalline substance, fusible at 300°, and very sparingly soluble in the ordinary solvents, has no poisonous effect upon dogs even in daily doses of 5 grms. Malonanilic acid, which may be regarded as an acetanilide in which a hydroxyl of the methyl-group is replaced by carboxyl, melts at 135°; it crystallises in transparent laminæ, and is readily soluble in

ether, alcohol, and water. The sodium salt of malonanilic acid has been found perfectly inactive in febrile affections. Paraphenacetine-carbonic acid, a phenacetine substituted with carboxyl, melts at 134°, crystallises in rhombic needles, is readily soluble in alcohol, but sparingly in water. Whilst phenacetine exerts well-known characteristic effects, capable of therapeutic utilisation, phenacetine-carbonic acid is perfectly inert.—*Archiv. de Sciences Biologique de St. Petersburg* and *Chemiker Zeitung*.

ON THE VOLUMETRIC DETERMINATION OF SULPHURIC ACID IN SULPHATES.

By PROF. A. VON ASBOTH.

E. STOLLE recently proposed in the *Chemiker Zeitung* a method for the volumetric determination of sulphuric acid. Barium chromate dissolves in hydrochloric acid according to the equation—



and from this solution ammonia precipitates all the chromic acid as neutral barium chromate.

A hydrochloric solution of barium chromate is used for the precipitation of the sulphuric acid; there is thrown down on supersaturation with ammonia a quantity of barium chromate corresponding to the barium still remaining in solution, whilst the residue of the chromic acid remains dissolved. This chromic acid, still in solution, is titrated after acidulation by sulphuric acid with a solution of ferrous oxide, using potassium ferricyanide as indicator. This chromic acid is the direct measure for the sulphuric acid present.

Prof. von Asboth being in want of a rapid method for the determination of sulphuric acid tested this process at once. The solution of barium chromate was prepared as directed, particular care being taken that neither barium chloride nor potassium chromate remained in solution. For the analysis he used chemically pure potassium sulphate. The first analysis was executed 24 hours after the preparation of the solution of barium chromate. The author obtained 87.00 per cent K₂SO₄; in the afternoon of the same day he found 86.80 per cent K₂SO₄, and five days afterwards the method indicated only 55.10 per cent of K₂SO₄.

The solution of barium chromate in the bottle, after standing for some time, gave off a strong smell of chlo-

vine. This odour gave at once the explanation. A part of the chromic acid, or we may say of the barium bichromate, passes into decomposition in contact with hydrochloric acid, with the formation of chlorine and probably chromium chloride along with the barium chromate. As a part of the chromic acid is already decomposed on supersaturation with ammonia, there remains barium chloride in solution. This barium chloride eliminates one part of the sulphuric acid, and as we calculate the quantity of sulphuric acid from the chromic acid which has passed into solution, it is plain that we always obtain less sulphuric acid than is actually present. The longer the solution of barium chromate is kept the more chromic acid is decomposed and the less sulphuric acid will be found. As a proof that these suppositions are correct the author has prepared neutral barium chromate, and washed the precipitate until the filtrate no longer gave the reactions for barium chloride. The precipitate was dissolved in dilute hydrochloric acid and set aside for 24 hours. After the supersaturation a part of the solution was treated with ammonia and barium chloride was found in the filtrate.

From these experiments it follows that Stolle's method is not available for the volumetric determination of sulphuric acid. Perhaps neutral barium chromate might be kept in store in a moist condition, and the solution of barium chromate might be prepared afresh for every analysis. The decomposition would then not occur.—*Chemiker Zeitung*.

DETECTION AND DETERMINATION OF METALLIC LEAD AND LEAD COMPOUNDS IN COMMERCIAL TARTARIC AND CITRIC ACIDS.

By M. BUCKET.

BOTH the tartaric acid and the citric acid of commerce are often contaminated with metallic lead and compounds of this metal due to their preparation in leaden vessels. For the determination of the metallic lead we dissolve 200 grms. of the acid in question in three times its weight of water, and add ammonia in slight excess, so as to effect the perfect solution of any crystalline lead sulphate which may be present. After the lapse of 24 hours the liquid is decanted off and set aside; the precipitate formed is collected on a filter, carefully washed, and dissolved on the filter with nitric acid.

The nitric solution is concentrated and mixed first with sulphuric acid, and then with twice its volume of alcohol. The precipitate of lead sulphate is washed with alcohol, dried, ignited, and weighed. The solution of ammonium citrate (or tartrate) first obtained serves for the determination of the compounds of lead; the solution is acidulated with hydrochloric acid, precipitated with sulphuretted hydrogen water, and determined as lead sulphate as above.—*Repert. Pharmac. and Chemiker Zeitung*.

DETERMINATION OF SULPHUR IN FUELS BY ESCHKA'S PROCESS.

By DR. FRANZ HUNDESHAGEN.

THE method of Eschka, much recommended for the determination of sulphur in coal and other solid combustibles, consists in burning the substance in presence of sodium carbonate and magnesium oxide. The author recognises that a serious error may manifest itself in the application of this process, in consequence of the production of gaseous sulphur-compounds which escape condensation by the reagents employed. This loss, which may reach 6 per cent and more of the total sulphur, is essentially

due to a formation of sulphuretted hydrogen. It is easy to ascertain this by placing at the mouth of the crucible a paper moistened with a solution of lead.

We may escape this loss entirely, or almost entirely, by substituting in Eschka's mixture potassium carbonate for sodium carbonate. Hundeshagen finds that a mixture of one part dry potassium carbonate with two parts by weight of magnesium oxide is most advantageous in all places.

If we increase the proportion of potassa the mass becomes fritted at a red heat and the combustion of the coal is impeded. To one part of coal we use at least two parts of the above mixture; three-fourths of the reagent are intimately mixed with the finely-powdered coal, and the remaining one-fourth is spread at the top. The combustion proceeds more rapidly than with the soda mixture, and is generally completed in from a quarter to half an hour.

The inconvenience of Eschka's mixture is due in the first place to the property of sodium carbonate to become completely dehydrated at a low temperature, and to possess in this state only a very feeble power of absorbing sulphuretted hydrogen, &c.; and further, sodium sulphide is easily decomposed by moist carbonic anhydride.

The advantages of potassium carbonate lie in its power of fixing water even at a rather high temperature, and to react with sulphuretted hydrogen to form potassium hydrosulphate with an escape of carbonic anhydride.

This absorption of sulphuretted hydrogen is promoted by the fact that potassium carbonate, intimately mixed with magnesia, reacts partially with it under the action of watery vapour to form potassium hydroxide, the absorbent capacity of which for sulphur compounds is much superior to that of the carbonate. Sodium carbonate does not possess this property, or at least only in a very slight degree.

We may easily demonstrate the difference of action of the two alkaline carbonates with sulphuretted hydrogen. Sodium carbonate mixed intimately with a slight proportion of sodium sulphide and bicarbonate, or with ammonium sulphide, gives off a considerable quantity of sulphuretted hydrogen, especially if exposed to heat, whilst a very small addition of potassium carbonate, if intimately incorporated with the other ingredients, completely hinders this escape.—*Chemiker Zeitung*.

NOTICES OF BOOKS.

The Analytical Chemistry of the Fatty Substances. (Chimie Analytique du Matières Grasses.) Methods for the Assay and the Analysis of Oils, Tallows, Greases, Glycerines, "Turning" Oils, Butters, Waxes, Resins, &c. Examples of Analysis—Reports. By M. FERDINAND JEAN, Director of the Laboratory of the Commercial Exchange, Chief of the Laboratory of the French Society of Hygiene. Paris: Edmond Rousset et Cie. 1892. Large 8vo., pp. 636.

THIS elaborate work is founded upon a former publication of the author and M. Dalcan, on the chemical methods used for determining the commercial value of oils and fats. Subsequently the author has devoted much attention to the examination of new methods for the analysis of these substances. In so doing he has utilised the exceptional facilities afforded by his official positions, and has studied critically the principal works on the subject which have latterly appeared. The result has been the present excellent volume.

The author confines himself to practical data concerning the assay and analysis—how does he draw a boundary line between these operations?—whilst leaving untouched the extraction and purification of the substances in question. He is fully sensible of the difficulty of the

subject. He declares that "all the science of the sophisticator consists in producing mixtures which with Lefebvre's oleometer present the specific gravity of pure oils." This, he tells us, is the sole means of control employed, even by the Commission on Oils of the Chamber of Commerce. At present it is rare for an absolutely pure oil to be obtainable in open market. Consequently their true characteristic properties can be determined only by chemists who possess exceptional opportunities. The colour-tests he rightly considers uncertain and variable. He might have added that often the reactions are due not to the oil itself, but to natural impurities which may or may not be present.

Among the physical properties of oils he lays the chief weight on the specific gravity, the thermic degree (Maumené's process), and the optical deviation. These three determinations are sufficient in a majority of cases to ascertain the purity or impurity of an oil. These tests are reinforced by a variety of other methods. According to MM. Doumer and Thibaut, a study of the absorption spectra of oils enables us to divide them into four categories. These authors experimented on expressed oils prepared at temperatures not exceeding 60°, the strata examined having been 12 m.m. in thickness.

The first class has the spectrum of chlorophyll. It includes the oils of olive, nuts, and hemp-seed. The spectrum of nut-oil has little luminosity, but the blue and violet bands are distinct.

The oils of sweet and bitter almonds and castor-oil have no spectrum.

On the contrary, colza, rape, linseed, and mustard oils absorb all the chemical radiations. The spectrum, instead of extending towards the blue, indigo, and violet, and gradually fading, ceases abruptly in the middle of the green.

The last category includes the oils of sesame, earth-nut poppy, colza, and cotton-seed, as characterised by three bands in "the chemical portion of the spectrum. It displays neither the green, orange, nor red bands characteristic of chlorophyll.

Among the physical methods described we find the determination of the electro-conductivity of oils (Rousseau's diaphragm), and the oleographic method of Tomlinson and Moffat, which latter is described in full.

The optical analysis by means of the oleo-refractometer of E. H. Amagat and the author is described *in extenso*, with the useful addition of a table showing the deviations of the principal oils, crude and purified, and of sophisticated samples.

The Maumené process, as effected with the aid of the thermolæometer and with the improvement suggested by Ellis, is fully appreciated.

The determination of the chemical characteristics of the fatty bodies forms the subject of the third chapter. Here we find an account of the saponification number (Kœttstorfer's test), Hehner's number, Reichart-Meissl-Wolff's number; the iodine number (Hübl's), the bromine number, the acetyl and the nitryl numbers.

The colour reactions are not omitted, though the author's confidence in them is not unlimited.

As an instance showing how thoroughly the characteristics of the several oils are described, we take one of them at random—earth-nut oil. Firstly come its synonyms, in French, Latin (for the benefit of the pharmacists), German, and English. Then follow its specific gravity at 15° correction for temperature; degree of the oleo-refractometer; Maumené's degree; congelation-point; specific gravity of the fatty acids at 100°; fusion and solidification-points of the fatty acids; iodine number; Hehner's number; bromine number; number of saponification, and acetyl number.

The detection of the sophistications of olive oil has been worked out with especial care.

The section on the Turkey-red oils, natural and artificial, is very satisfactory.

Our opinion of this work as a whole is extremely

favourable. It will prove of the highest utility to chemists engaged in any of the industries which make use of fatty matters and their products. We cannot, however, help noticing as a defect the want of an index. We regret, also, that the author has not seen his way to dispense with the vexatious hydrometric scale of Baumé.

Papers and Proceedings of the Royal Society of Tasmania for 1891. Hobart: Mercury Office.

We have on former occasions noticed, with a feeling of regret, that our colonial brothers, at the meetings of their scientific gatherings, occupy themselves too much with matters which might be as conveniently—to say the least—discussed in Europe, leaving untouched questions which can be dealt with only under the Southern Cross. Very much of the Report before us consists of matter of the former class. Not a single chemical paper seems to have been read before the Society.

Force and Mass. Formers of the Cosmos. Identity of the Material Forces. ("Kraft und Masse. Bildner des Kosmos. Identität der Naturkräfte.") By RUDOLF MEWES. Part I. Berlin: Klein and Co. 1892.

THIS pamphlet by its title at once reminds us of the celebrated "Kraft und Stoff" of Büchner,—a happier name had it not been pre-engaged.

The author commences with a long and decidedly polemical preface. Herr Mewes remarks that the heads of the great publishing houses, before accepting a scientific work, take the opinion of the University professors, who do not feel themselves in a position to recommend books not drawn up from their own point of view. Hence the most "epoch-making" works are liable to be rejected, and owe their appearance to some fortunate accident. If we may venture to make a suggestion to *savants* who have not yet become popular, but who have—or believe that they have—arrived at some novel and important generalisation, we should advise them in drawing up a memoir or a pamphlet to place their theory or their generalisation by itself in the plainest language and in the fewest possible words, either at the beginning or the end of their work. It should be given in such a manner that "he who runs may read." Above all things it should be disentangled alike from metaphysical speculation and from mathematical formulæ. Having thus stated, *totidem verbis*, what they seek to prove, they should proceed to its demonstration and its illustration in such manner as they think most suitable.

Herr Mewes, in this the first part of his treatise, discusses the absorption and emission of the vibrations of the ether, the radiation of the waves of the ether, and the propagation of the ether waves of conduction. It is possible that in his second part he may proceed to answer the questions which his readers will long to put.

Concerning thermo-chemistry he declares that in its present form it has effected no essential advance for the principles of theoretical physics. "It is still involved in the old representations, and in the manner of the chemists of the old school it regards chemical processes as the effects of chemical affinity."

We look forward with interest to the second portion of this treatise, in which the author's conclusions may be expected to assume a crystalline form.

Chemical Theory for Beginners. By LEONARD DOBBIN, Ph.D., and JAMES WALKER, Ph.D., D.Sc., Assistants in the Chemistry Department, University of Edinburgh. London: Macmillan and Co., 1892. Small 8vo., pp. 236.

THE authors of this little work point out that the principles of chemistry—as compared with isolated facts—are too generally neglected in text-books, whether of smaller or larger dimensions. From the use of the smaller

manuals the student seldom obtains any satisfactory grasp of chemical theory, whilst in the more advanced treatises "the same subjects not unfrequently receive similar scant attention, because the student is supposed to have been introduced to them already." This complaint is not entirely unfounded. We can therefore express our satisfaction with the attempt made by Drs. Dobbin and Walker to set forth facts in combination with the theories to which they have led.

There is another feature in this work which deserves, we think, favourable consideration,—the entirely non-mathematical treatment of the more important principles of general chemistry. It is admitted that not a few important conclusions could never have been reached without the aid of the higher mathematics. But we submit that the results when thus reached may be expounded and dealt with in the absence of such methods. It would be vain to attempt to erect a cathedral or a palace without the intervention of scaffolding and ladders. But when the structure or any portion of it is completed, these auxiliaries are removed before it is thrown open to the inspection of the public.

We make these remarks because it is an error to assume that every man capable of doing service in Science must necessarily be a mathematician, or be capable of being trained to use mathematical methods. We therefore trust that the experiment of the authors may prove successful.

Agricultural Chemistry. A Familiar Explanation of the Chemical Principles Involved in the Operations of the Farm. By ALFRED SIBSON, F.C.S., Analytical and Consulting Chemist. With a Preface by the late Dr. AUGUST VOELCKER, Consulting Chemist to the Royal Agricultural Society. Revised, extended, and brought up to date by the AUTHOR and A. E. SIBSON, F.C.S. London, Manchester, and New York: G. Routledge and Sons, Limited, 1892. 8vo., pp. 348.

The first edition of this book has long been favourably known to farmers. The present issue has been enriched with novel matter, especially on reverted phosphates, slag phosphates, sewage manures, ensilage, &c. On these subjects the views of the authors will not always be accepted without question. The Messrs. Sibson evidently set a higher value upon farmyard manure than is done by M. Ville and his school. They advance the opinion that farmyard manure is "the most economical source on which the farmer must rely for sustaining the fertility of his land," and that it is "the most complete, most valuable, and only perfect manure," and that "this substance only can return to the ground all the materials removed by cultivation." These, to say the least, are very strong statements. But farmyard manure contains at the least 90 per cent of matter which is useless, or which is fully supplied by the atmosphere and the rain, all which involves labour in conveying to the fields and spreading. If the soil is poor in any of the chief constituents of plant food, the farmyard manure obtained from its produce will obviously be deficient in that constituent, and will not improve land of the same quality.

Upon sewage manures the authors are disposed to be severe. On due inquiry they would find that sewage manure can be dried down to 14 or 15 per cent of moisture without the injurious addition of lime, and that it contains without any "fortification" 3 per cent of ammonia and 5 per cent of phosphate. Such a sewage manure is certainly far richer than farmyard manure. Of course the process now perpetrated in London of first precipitating the sewage and then carrying it out to sea is utterly deplorable, and fully justifies Messrs. Sibson's remark about the expenditure of millions to get rid of it. Almost equally to be condemned is the scheme here called "ingenious," of burning the sewage sludge, for converting it into cement. The sludge is mixed up with the materials necessary for producing cement and burnt.

But it adds nothing to the valuable properties of the cement, and all the manurial constituents are simply wasted just as much as if they had been turned into the sea.

Sewage-irrigation is of course an excellent expedient in climates such as South Africa, Australia, many parts of India, &c., where the rain-fall is either scanty or very intermittent. But in so cold and drizzly a region as England the case is very different.

It is very questionable whether in wet seasons the "Gillwell harvest saver" is not after all preferable to the silo. It was perhaps unfortunate that the harvest saver obtained the gold medal of the Society of Arts, between which body and the Royal Agricultural Society very little love is said to be lost. The harvest saver is applicable also to grain, which the silo is not.

Broadly considered, however, the teachings of the work before us will be very valuable to the farmer.

A Lecture Course in Elementary Chemistry. By H. J. LILLEY, M.A. London: Simpkin, Marshall, and Co.

This is another of those small elementary works which have been so numerous during the past twenty years. It contains substantially the same matter and suggests the same questions. The author does not, as far as we perceive, indicate any especial *raison d'être* for his work, or point out any feature which is not common to other treatises of the same class.

The following passage may be pronounced misleading: "Sodium and potassium salts impart a lilac and yellow colour respectively to a flame in which they are vaporised." The words "lilac and yellow" require to be placed in an inverted order, since a pupil reading the passage as it stands might carry away the impression that sodium salts give the lilac and potassium salts the yellow colour.

Mention is elsewhere made of Pettenkofer's suggestion of the use of hydrogen peroxide for restoring oil-paintings. Unfortunately this expedient has proved unsafe; sometimes it fails, and in others it destroys the picture altogether.

There is no mention of spectral reactions as a means of chemical diagnosis.

CORRESPONDENCE.

CHARLES BELL (DECEASED).

To the Editor of the Chemical News.

SIR,—Kindly insert the following advertisement in your next issue:—

BELL, CHARLES.—Would any friend or relation of Mr. Charles Bell, of London, Copper Assayer, kindly communicate with Karl Renouf, Linden Villa, 29, St. Saviour's Road, Jersey.

In sending you the above I should like to add some further facts for your information, in case you might kindly see your way, through your columns or otherwise, to give me any hints or suggestions.

The Charles Bell in question has recently died abroad, and left no clue to his relations, and, as his only known correspondent, I have been communicated with.

My knowledge is limited to the fact that I was a fellow traveller with Mr. Bell during last May, when we met at Marseilles, and he then informed me that he had been with a firm of assayers in London, and had just come from Spain, whither he had gone at the request of a Spanish copper mining company to test some copper ore at the mines.

I believe he was then on his own account, and that the mining company paid his expenses. This I do know,

that he found the lode very rich, even richer than he expected, as the company had sent him a sample to London, but the one he himself drew from the mines was still better.

Unfortunately he never told me the name of this mining company, or that of the firm of assayers with whom he had been when in London. I have applied to several well-known assayers for news, but without success, and I therefore send you the advertisement, trusting it will reach the eye of someone who knew Mr. Charles Bell who will communicate with me.—I am, &c.,

KARL RENOUF.

Linden Villa, St. Saviour's Road,
Jersey.

ON THE ORGANISATION OF SCIENCE.

To the Editor of the Chemical News.

SIR,—While thanking you for your sympathetic review of my pamphlet, I must ask your permission for space to point out that one paragraph in your review is calculated to cause some little misapprehension; for you say that "upon one important point" (viz., the "dissociation of the Literary and Philosophical societies of our large provincial cities") "the author does not touch." If you will do me the favour to refer to pp. 21—23, you will see that I have discussed this question, and have strongly advocated that all these provincial Philosophical and Royal societies, which receive papers upon a dozen different subjects, should "cease to exist as such" (p. 22), and resolve themselves into local sections of the Physical, Chemical, Linnean, Geological, and other societies. It being suggested that all these London societies should form local sections on the model of the Chemical Industry Society. I admit, however, that I have said nothing as to the literary side of these societies, and that presumably led to your reviewer's remarks.

(I hope that I shall not raise a hornet's nest by suggesting—but, anyhow, I must take the risk—that the various provincial Philosophical and "Royal" societies alluded to above should cease to exist as such. . . . Let them dissolve; they will have done their work, and done it well; but they must not stand in the way of better organisation of science."—Page 22).

Apologising for trespassing on your space.—I am, &c.,
"A FREE LANCE."

London, Sept. 24, 1892.

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—I observe in the current number of the CHEMICAL NEWS a paper by Mr. William Johnstone, who styles himself "Emeritus Fellow of the Institute of Chemistry."

I beg to inform you that Mr. William Johnstone is not a Fellow of the Institute, and that no such title as Emeritus Fellow of this Institute exists.

Mr. Johnstone was a Fellow of this Institute, but his name was recently removed from the Register by the Council; such removal was not upon a ground involving any imputation upon his professional capacity or personal character, but upon the view of the Council on the professional conduct of the plaintiff on one occasion.

Mr. Johnstone brought an action against the President and Members of the Council, in which he sought to prevent the removal of his name from the Register and claimed an injunction and damages. The action was settled in Court, the record being withdrawn without costs on either side upon Mr. Johnstone undertaking not to use in future the title of Fellow or Member of the Institute.—I am, &c.,

G. H. ROBERTSON,

Registrar to the Institute of Chemistry.

9, Adelphi Terrace, Strand, W.C.
Sept. 28, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., Nos. 9 and 10.

These numbers contain no chemical matter.

Vol. cxv., No. 11, September 12, 1892.

Combustion-Heat of Glycolic Acid.—M. Berthelot.—The conversion of acetic acid into glycolic acid disengages +40.2 cal. in place of +20.6, and the change of acetic acid into glyoxylic acid gives +79.4 cal. or 39.7×2 . This rectification removes an anomaly.

Ptomaine obtained by the Culture of Micrococcus Tetragenus.—Dr. A. B. Griffiths.—This micrococcus is quickly isolated from the sputa of phthisical patients; its elements are spherical cocci of from 1μ to 1.5μ in diameter. It is easily cultivated upon all media. If pure cultures of this microbe are cultivated for several days upon peptonised gelatin a ptomaine is produced. It is a white, crystalline solid, forming prismatic needles. It is soluble in water with a slightly alkaline reaction; it forms a hydrochlorate, a chloraurate, and a chloroplatinate all crystalline. It is also precipitated by the phosphomolybdic, phosphotungstic, and picric acids. Nessler's reagent gives a green precipitate; tannic acid a maroon precipitate, which is slightly soluble. Its composition is $C_5H_6NO_2$. It is poisonous, occasioning death in 36 hours.

On Echinochrome: a Respiratory Pigment.—Dr. A. B. Griffiths.—In 1883 Dr. McMunn discovered a brown pigment in the perivisceral fluid of certain Echinoderms (*Echinus esculentus*, *Strongylocentrotus lividus*, &c.). This pigment, which he named echinochrome, has a respiratory function. It exists in two states: as oxyechinochrome charged with active oxygen, and reduced echinochrome deprived of active oxygen. Dr. Griffiths assigns to echinochrome the empirical formula—



It is partly soluble in water and in alcohol. If boiled with the mineral acids it is transformed into hæmatoporphyrine, hæmochromogene, and sulphuric acid. It possesses certain characters analogous to those of hæmoglobine and chromocruorine.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 12.

Novel Salts of Iron.—Marcel Lachaud and Ch. Lepierre.—The author's general manner of operating is as follows:—He melts 1 mol. ammonium sulphate and 1 mol. H_2SO_4 up to tranquil fusion (121°). Into the liquid he throws about one-fifth of ferrous sulphate or of ferrous ammonium sulphate, dry, or preferably hydrated, in which latter case the crystals obtained are finer. He heats gently to expel the greater part of the water, and continues the heating more or less according to the case, watching the progress with the microscope. There are formed successively several crystalline salts, chiefly insoluble in cold water, which nevertheless attacks them by degrees. The action of hot water is more rapid. To separate these bodies from the excess of ammonium sulphate he casts them in plates, which are allowed to cool, and coarsely powdered; the powder is boiled with an ascending condenser with an equal weight of alcohol; the mass is disaggregated. The hot alcohol is decanted off, having dissolved the acid salt, which crystallises out in fine laminae. The alcoholic treatment is repeated if necessary, and the product is centrifuged or filtered rapidly to separate the alcohol.

Action of the Alkaline Nitrites upon the Ethers of the Monobromic Fatty Acids.—G. Lepercq.—M. Steiner has shown that a mixture of ethyl monochloroacetate and of potassium nitrite under the influence of a gentle heat gives off nitrogen, nitric oxide, and carbonic acid, whilst potassium ethyloxalate is formed. The author seeks to show that this salt is not the sole product of the reaction, and that there is likewise formed a nitrogenous body.

On Diamidosulphobenzide and some of its Derivatives.—Ch. Lauth.—Diamidosulphobenzide,—



readily yields diazo-derivatives by the action of nitrite in presence of hydrochloric acid; and these derivatives, if treated with the usual reagents, produce beautiful colouring matters, oranges, scarlets, and browns. Brown and violet tetrazo-colours may also be obtained. The various colouring-matters, notwithstanding their beauty, present no important advantages over the products already known, and they have but slight affinities for cotton.

Volumetric Determination of Uric Acid in Urine.—E. Deroide.—The compound of uric acid and of silver has a constant composition, and if we eliminate the xanthic compounds the Haycraft-Herrmann process will be preferable to all others.

New Preparation of Fatty Bromo-Acids.—P. Genviessé.—The author has obtained by his method monobromo-acetic acid, the dibromo-compound, the α -monobromo-propionic acid, and the normal α -monobromo-butyric acid.

Certain Properties of the Alkaline Earthy Metals.—L. Maquenne.—The author uses in his experiments the amalgams of the alkaline-earthy metals. He obtains barium nitride, N_2Ba_6 , barium carbide, C_2Ba , strontium nitride, N_2Sr_3 , and calcium nitride, N_2Ca_3 .

Zeitschrift für Analytische Chemie.
Vol. xxx., Part 6.

Examination of Etheral Oils.—A collection of paragraphs for which we must refer to the original.

Turkey Red Oil.—Arthur Wilson.—From the *Journ. Soc. Chem. Ind.*

Determination of Ferric Oxide and Alumina in Phosphates.—R. Jones (*Zeit. Angew. Chemie*).—This paper will be inserted in full.

Determination of the Pentaglykoses in Plants.—W. E. Stone.—From the *Ber. Dcut. Chem. Gesell.*

Identification of Phenacetine.—W. Autenrieth and O. Hinsberg (*Archiv. der Pharm.*).—If phenacetine in fine powder is covered with nitric acid at 10 or 12 per cent and heated to ebullition for a short time, the liquid takes a yellow or orange colour, and the substance previously colourless is converted into an intensely yellow nitro-compound.

Reactions of Piperazine.—H. Eckenroth (*Pharm. Zeit.*).—With Nessler's reagent it gives a white, with copper sulphate a blue, with cadmium chloride a white, precipitate, with silver nitrate nothing.

Determination of the Alkalinity of Blood.—Before and during coagulation the alkalinity is less perceptible. The addition of sodium sulphate to prevent coagulation does not affect the reaction.

Quantitative Determination of Cholesterine.—K. Obermüller.—A method for the separation of cholesterine from fat.

Detection of Sugar and Carbohydrates in Urine.—M. Jastrowitz (*Deutsch. Medicin. Wochenschrift*).—The urine of the dog, the horse, and the rabbit, are found to contain carbohydrates, and are in a slight degree levo-rotatory.

Diagnosis of the Xanthine Substances of Urine.—G. Salomon (*Archiv. Path. Anatomie*).—With an excess of soda-lye, hypoxanthine, xanthine, and guanine, form readily soluble compounds, whilst para- and heteroxanthine yield compounds readily soluble in an excess of the precipitant.

Detection and Determination of Albumen in Urine.—J. A. McWilliam.—From the *British Medical Journal*.

Detection of Arsenic.—C. H. Wolff (*Pharm. Central Halle*).—The author has developed the electric method of Klobulow. The hydride is decomposed by means of the induction spark.

Delicacy of Various Reactions for Arsenic.—C. O. Curtmann.—The Gutzeit reaction in 1 c.c. of a liquid containing 0.0001 mgrm. As_2O_3 gave in an hour no yellow spot. If the quantity of arsenic was 0.001 mgrm. a yellowish spot appeared after the lapse of twenty-five minutes. Hume's reaction gave with silver nitrate and ammonia a precipitate only after six minutes. The gas given off by Fleitmann's process acted upon silver nitrate paper only after thirty minutes.

Determination of the Atomic Weight of Osmium.—K. Seubert (*Liebig's Annalen*).—The author's mean result was $\text{Os} = 190.33$.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vii., No. 77.

On Malting and on Brewing Beers for Keeping.—Ernst Saalfeld.—From the *Transactions of the Institute of Brewing*.

MISCELLANEOUS.

The Institute of Chemistry.—An Extraordinary General Meeting of the Institute of Chemistry of Great Britain and Ireland will be held at 9, Adelphi Terrace, Strand, on Friday, the 7th day of October, at 5 p.m., to receive, and if desirable approve, of the following Report of the Finance and Office Committees which has been adopted by the Council:—

"*Report of the Finance and Office Committees.*—In view of the necessity for providing, in addition to office accommodation, premises upon which the Examination of the Institute can be efficiently conducted, the Finance and Office Committees jointly recommend that the Office Committee be empowered to take steps to secure such premises; and, if necessary, to expend upon the purchase of a lease a sum not exceeding one-fourth of the invested capital of the Institute, and that the President be authorised to sign the necessary documents."

The Spontaneous Oxidation of Humic Acid and Vegetable Mould.—M. Berthelot and G. André.—The progressive elimination of the humic matters of the soil explains the necessity of its incessant renewal by the decomposition of plants and the addition of dung. The total arable soil behaves like a living being submitted to perpetual destruction and renewal.—*Bull. Soc. Chim. de Paris*, Series 3, No. 13.

Microbia at Sea.—According to an eminent medical contemporary, though the atmosphere in mid-ocean is free from microbia this is not the case on board ship. In the state-rooms and in the first and second cabins of the steamer—evidently a "liner" plying between Europe and America—many bacteria were found on short exposures, especially in the saloons after dining hours. In the steerage, where there were 1100 emigrants packed together in filth, many thousand bacilli and micrococci came to luxuriant development on agar plates and in large gelatin tubes.

Scandinavian Congress of Naturalists.—According to the *Chemiker Zeitung* this meeting was this year held at Copenhagen under the presidency of Prof. Julius Thomsen. The Chemical Section elected as its president Prof. P. T. Clève, and as its vice-presidents Prof. O. Pettersson and Prof. S. M. Jørgensen. The principal papers read before the section were "Some Double Haloid Salts of Gold," by Dr. E. Petersen. The compounds Au_2Cl_4 and Au_2Br_4 obtained by Thomsen, but declared non-existent by Krüss and Schmidt, exist in reality. Julius Petersen reported on the physical conditions of the metal-ammonium compounds. Prof. P. T. Clève delivered a discourse on substitutions in the naphthalene series, and gave a historical survey of Kekulé's benzol-formula. Dr. K. Ström discussed the behaviour of isopropylalcohol with sodium ethylate. Prof. S. M. Jørgensen communicated results on certain cobalt-tetramine salts. Prof. H. Kjeldahl reported on the optical rotatory power of certain vegetable albumenoids. H. Schjerwing, the manager of the Ny Carlsberg Brewery Laboratory, communicated researches on certain derivatives of phenylhydrazine. W. Cronquist reported on the examination of explosives, and on the melting-point of paraffin. Prof. O. Pettersson discussed the proportion of carbonic acid in the air, and a method of determining the alcohol in fermented liquids. Herr Larson gave a full account of recent improvements in the production of copper. Dr. A. Langlet described his investigations on some azthine derivatives. Dr. O. T. Christensen doubted the existence of manganese alum. Herr Franke is of the same opinion. Candidate Schleisser reported on the preparation of diazoamido-benzol and on hardening gypsum. Dr. Emil Petersen treated of the electrolytic dissociation-heat of some feeble acids.

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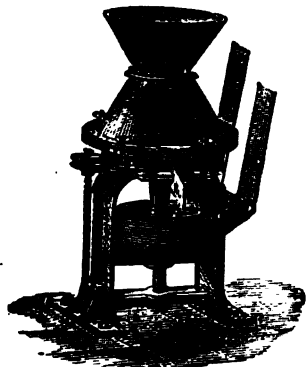
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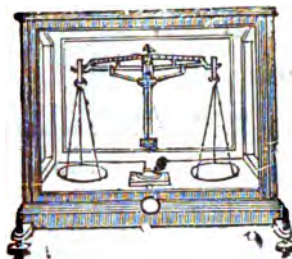
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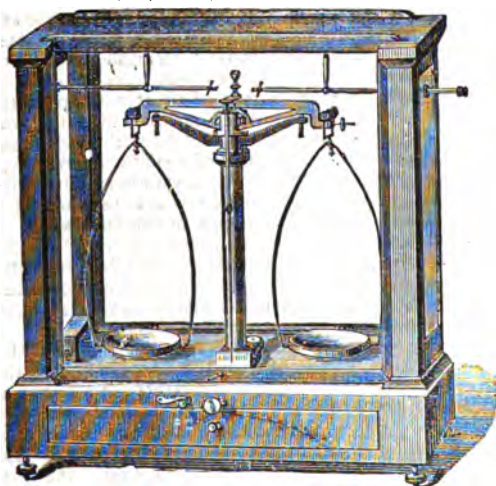


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VOL. LXVI., No. 1715.

THE CONDITIONS OF THE FORMATION AND DECOMPOSITION OF NITROUS ACID.*

By V. H. VELEY, M.A.

Introductory.

THROUGHOUT the whole science of chemistry there is possibly no reagent so frequently represented as taking part in various transformations, but of which so little definite is known, as nitrous acid. In many text-books its properties are cursorily discussed in a few lines, while some writers have gone so far as to deny its existence altogether even in the presence of nitric acid. Among the commoner examples of reactions considered to be effected by nitrous acid, it is necessary only to mention the conversion of the primary paraffinoid amines into the corresponding alcohols, the formation of nitroso- and diazo-derivatives, and the preparation of the fulminates. In a previous paper (*Phil. Trans.*, 1891, A, pp. 312-313), it was my endeavour to prove that the solution of certain metals in nitric acid was conditioned by the presence of nitrous acid, and the cause of the chemical change explained on the supposition that the acid is alternately formed and decomposed.

As a fitting corollary to these investigations, it seemed worthy of interest to examine to some extent the validity of this hypothesis by endeavouring to imitate the reactions supposed to take place on solution of the metal, either when no metal is present, or when the metallic salt is either present or absent.

The stability of nitrous acid in presence of nitric acid forms also a part of this research, and, conversely, the stability of nitric acid in absence of nitrous acid is discussed.

In the present, as in my former, investigations, it will be understood that the term nitrous acid is applied to that kind of matter which decolourises potassium permanganate, liberates iodine from potassium iodide, and gives various colour reactions with certain organic bases.

The Formation of Nitrous Acid in Nitric Acid Solution.

Nitrous acid is generally produced directly by the decomposition or reduction of nitric acid effected (1) by heating the acid, (2) by passing nitric oxide or nitrous fumes into it, (3) by electrolysis, or more indirectly (4) by addition of nitrogen peroxide to water; and (5) by decomposition of metallic nitrites with acids. The nature of these several changes, their conditions, and the compositions of the solutions obtained form the main subjects of this investigation.

The Methods of Analysis.

The following process was adopted for estimating the respective amounts of nitrous and nitric acids in presence of one another; the total acidity was determined in the usual manner by means of standard alkali, the nitrous acid by means of potassium permanganate; from the factors thus obtained the amount of acidity due to the nitric acid by itself could be readily calculated. It was found by experience not only in the present but also in previous investigations, that nitrous acid could not conveniently be estimated by the addition of the permanganate solution until it is no longer decolourised, for the oxidation of the nitrous acid at the end of the operation is gradual and not instantaneous. This point does not seem to have been noticed by the writers on quantitative

analysis. Accordingly the method was modified as follows:—The solution of the nitrous acid was added to such a quantity of the standard permanganate, acidified with sulphuric acid, which was judged to be in slight excess over that required to complete the oxidation, and the whole mixture allowed to stand in stoppered bottles for half an hour. The pink liquid was then poured into potassium iodide solution, and the amount of iodine liberated by the excess of the permanganate determined, as customary, by standard sodium thiosulphate solution. There was apparently no risk of any of the nitrous acid escaping oxidation, and thus liberating iodine from the potassium iodide, if the method was carried out as described.

In order to test the accuracy of the process, some purified silver nitrite was re-crystallised several times from water, a known quantity of it was weighed out, suspended in water, and decomposed by a slight excess of purified sodium chloride. The amount of nitrous acid calculated as (NO_2) was determined in the solution, and for a test analysis the following may be cited:—

Amount of (NO_2) in 1 c.c. calculated from the weighed quantity of silver nitrite taken	0.005963 grm.
Amount of (NO_2) in 1 c.c. found	0.005974 "

The process is therefore accurate in this particular case to within 1 part in 600. When smaller quantities of nitrous acid were to be estimated, the metaphephenylenediamine method was adopted, the colouration produced being compared with a solution containing a known quantity of nitrous acid by means of the form of tintometer described in my former paper (*vide supra*).

The Stability of Nitric Acid.

It seemed worthy of investigation to determine the actual temperature at which traces of nitrogen peroxide begin to be formed in purified nitric acid, of different degrees of concentration; hitherto only general statements are given in the text-books.* Samples of acid of specific gravity 1.5 and 1.4 respectively were purified by the method of blowing a current of air at a temperature of 35°, and thus obtained quite colourless; the latter was diluted (1) with its own volume, and (2) with three times its volume, of water. An acid of specific gravity 1.33 was prepared by distillation of re-crystallised nitre with sulphuric acid, and the reddish-yellow acid thus obtained was re-distilled with an equal bulk of sulphuric acid. A number of attempts were made to render this acid colourless by a current of air or carbonic acid, but, notwithstanding several modifications, these proved unsuccessful. Recourse was, therefore, had to distillation *in vacuo* in an apparatus specially constructed of glass.

The method of operation was as follows:—The slightly yellow acid was placed in a distillation flask, and the receiver kept cooled by a freezing mixture; at a temperature of 45°, and under a pressure of 15 m.m., the acid passed over without any visible ebullition. After one-third of the liquid had been condensed, the receiver was changed, and the remainder distilled over; the first portions contained a greater part of the nitrogen peroxide. The second distillate was then re-distilled in the same manner, and thus a perfectly colourless liquid was obtained (specific gravity 0.0=1.541)† containing only

* Carius (*Ber. Deut. Chem. Gesell.*, 1870, p. 690) states that when pure nitric acid of specific gravity 1.51 is heated in sealed tubes to a temperature of 150° and upwards, a reddish-yellow liquid is produced, with evolution of oxygen and "nitrous acid gas;" above 250° the liquid contains such an abundance of nitrous acid that it gives a blue colour on addition of a small quantity of water, and on further dilution nitric oxide is evolved. Accordingly, the decomposition of the acid under these conditions is expressible by the equation $2\text{HNO}_3 = \text{N}_2\text{O}_5 + \text{O}_2 + \text{H}_2\text{O}$.

† I am indebted to my colleague Dr. J. Warts for loan of apparatus and assistance in this method of procedure, which both in his and my hands has proved more successful than the air (or carbonic acid), current method, usually described in the text-books, when acids of specific gravity greater than 1.5 are required perfectly

* A Paper read before the Royal Society, June 2, 1892.

0.011 m.grm. of nitrogen peroxide. Attempts to prepare an acid of greater concentration and more free from the peroxide proved unsuccessful.

In the following table are given the amount of nitric acid in 1 c.c. of each of the several samples.

Sample.	Amount of nitric acid in 1 c.c.	Spec. gravity 10/10.
I.	1.350 grms.	1.541
II.	1.1890 "	1.812
III.	1.0763 "	1.420
IV.	0.5183 "	not determined
V.	0.2563 "	"

For each experiment 10 c.c. of the acid were placed in a small piece of combustion tubing, which had previously been cleansed by being filled with concentrated nitric acid and allowed to stand for several hours, generally, over night. The tubes were then rinsed several times with water, and finally with water re-distilled from potassium permanganate. It was hoped that by this method all reducing substances might be completely destroyed. After introduction of the acid the tubes were quickly sealed up and then heated to various temperatures in water or paraffin baths. The experiments were conducted in dull and generally foggy weather, advantageous at least for them, as concentrated nitric acid is decomposed by direct sunlight. At the end of each experiment the 10 c.c. of acid were poured into 100 c.c. of water, and the amount of nitrous acid determined by the metaphenylenediamine method, as explained above; this is then reckoned in terms of nitrogen peroxide, the substance which imparts the yellow tint to the impure acid.

Sample of acid.	Temperature.	Time.	Nitrogen peroxide produced expressed as 0.001 m.grm. in 1 c.c.
I.	30°	90'	0.25
III.	"	"	2.9
IV.	"	"	0.51
V.	"	"	nil

These results show that whereas the amount of nitrogen peroxide present in the most concentrated acid is doubled by heating under the conditions described above, yet the amounts of this same impurity produced in the less concentrated acids are quite inappreciable. A series of other determinations were made at high temperatures, the results of which are given below.

Sample of acid.	Temperature.	Time.	Nitrogen peroxide present. 0.001 m.grm. in 1 c.c.
I.	58°	90'	0.27
III.	"	"	2.7
IV.	"	"	2.9
V.	"	"	not measurable

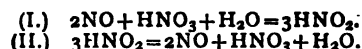
Sample of acid.	Temperature.	Time.	Nitrogen peroxide present.
I.	100°	90'	0.431
III.	"	"	0.05
IV.	"	"	nil
V.	"	"	nil
II.	120°	90'	0.96
III.	"	"	0.2
IV.	"	"	0.2
V.	"	"	nil
III.	155°	90'	0.70
IV.	"	"	0.06
V.	"	"	0.06
III.	195°	5'	2.19
IV.	"	"	80

* colourless. The distillation method, however, presents one of two alternate difficulties; on the one hand, in each repetition of the distillation the proportion of nitrogen peroxide is decreased; on the other, that of the water is increased.

It is manifest from the figures given in the tables above that sample No. I was decomposed to some extent at 58°, and to a greater degree at 100°, sample No. II. at 120°, sample No. III. at 155°, and very rapidly at 195°, sample No. IV. at 195°, while the most dilute acid remained practically unaltered throughout. It would also appear that, provided every care be taken to eliminate reducing substances, especially of an organic character, and provided also that the acids are not unduly exposed to sunlight, nitric acid is more stable than former experience indicated. It would be an interesting subject of inquiry to ascertain as to whether nitric acid is affected by shocks, as I have found that samples of acid purified so as to be practically free from nitrous acid were contaminated with that impurity after a railway journey.

Formation of Nitrous Acid from Nitric Oxide and Nitric Acid.

It is a common matter of observation that when nitric oxide gas is passed into nitric acid a greenish-blue solution is produced, which shows all the reactions of nitrous acid; some writers, however, consider that the nitric oxide gas is only dissolved as such in the nitric acid in that, when the liquid is warmed, the gas is again evolved. It is more probable that nitrous acid is formed and subsequently decomposed, changes represented by the following equations:—



Clemente Montemartini (*Rome, Accad. Lincei Rendiconti*, 1890, p. 264), has proved that of these changes the latter proceed quantitatively, at least in dilute solution, in accordance with the equation given.

If these changes are strictly reversible, it would follow as a necessary consequence that there would be a limit to the amount of the nitrous acid produced, and this limit would be dependent upon conditions such as concentration of acid and temperature. The equation for equilibrium will be—

$$p/q = \text{constant,}$$

wherein p is the mass of nitric acid, and q is the mass of nitrous acid, for when the limit is reached the amounts of nitric oxide gas passing in and out would be identical, while the alteration of the mass of water would be immaterial.

On the other hand, if the phenomenon is merely that of solution, the amount of nitric oxide gas dissolved should, other conditions remaining the same, diminish under all circumstances as the temperature increases.

To decide between these views, and to determine the limit, whether of nitrous acid formed or of nitric oxide dissolved, as the case might be, a series of experiments were conducted in the following manner.

Nitric acid was passed through an apparatus consisting of (1) a wash-bottle containing soda; (2) a set of Liebig's bulbs; and (3) a set of Geissler's bulbs both filled with nitric acid of the same concentration, the latter of which was used for the analytical determinations; and (4) a wash-bottle containing soda to prevent any nitrous fumes produced by the passage of the unaltered nitric oxide into the air, from accidentally coming in contact with the acid experimented upon. In these and succeeding experiments the apparatus consisted wholly of glass, except for small pieces of rubber tubing which served for connections; these were frequently renewed. Before the nitric oxide was passed, the whole apparatus was filled with hydrogen, my previous experiments having shown that this gas, when ready-made, does not reduce nitric acid, but even mechanically blows off any slight impurity of nitrous acid. At the end of the operation the Geissler's bulbs were quickly detached, and the acid blown out by a rapid stream of carbonic acid. While the experiment was proceeding the bulbs were kept in a water-bath, the temperature of which was carefully regu-

lated; the passage of the nitric oxide was kept as uniform as possible.

The following table contains the results of the first set of experiments; not only of the actual amounts of nitric acid, and of nitrous acid, *i.e.*, the reducing power, are given, but also of the percentage amounts of these acids, taking the total acidity as 100:—

SERIES I.—Temperature, 22.5°.

	Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage rates.
—	—	0.2549	nil	100:0
After passage of nitric oxide ..	4	0.2404	0.0168	93.47:6.53
" "	8	0.2409	0.0164	93.62:6.38

These results show that the phenomenon, whether of reaction or of solution, was complete at the end of the first interval of time; but, taken by themselves, they would not suffice to distinguish under which category the change is to be classified. Accordingly a series of experiments were conducted in which the only variable condition was that of temperature, for, as pointed out above, if the nitric oxide is merely dissolved, then the reducing power would diminish with increase of temperature, but if a chemical change takes place, then its amount would depend upon the relative intensities of the chemical change represented by the equations given.

SERIES II.—Temperature, 9°.

	Time. Hours.	Nitrous acid in 1 c.c. Grm.	Nitric acid in 1 c.c. Grm.	Percentage rates.
—	—	0.2549	nil	100:0
After passage of nitric oxide ..	3	0.2496	0.0169	93.66:6.34

SERIES III.—Temperature, 27.5°.

	Time. Hours.	Nitrous acid in 1 c.c. Grm.	Nitric acid in 1 c.c. Grm.	Percentage rates.
—	—	0.2549	nil	100:0
After passage of nitric oxide ..	4	0.2336	0.0171	93.18:6.82
" "	8	0.2362	0.0169	93.69:6.31

SERIES IV.—Temperature, 32°.

	Time. Hours.	Nitrous acid in 1 c.c. Grm.	Nitric acid in 1 c.c. Grm.	Percentage rates.
—	—	0.2549	nil	100:0
After passage of nitric oxide ..	3	0.2318	0.0223	91.22:8.76

SERIES V.—Temperature, 42°.

	Time. Hours.	Nitrous acid in 1 c.c. Grm.	Nitric acid in 1 c.c. Grm.	Percentage rates.
—	—	0.2549	nil	—
After passage of nitric oxide ..	3	0.2372	0.016	93.68:6.32

SERIES VI.—Temperature, 52°.

	Time. Hours.	Nitrous acid in 1 c.c. Grm.	Nitric acid in 1 c.c. Grm.	Percentage rates.
—	—	0.2549	nil	—
After passage of nitric oxide ..	3	0.2366	0.0136	94.56:5.44

It will be evident from the above experiments that the ratio of nitrous to nitric acid increases slightly with rise of temperature up to 32°, but from this point it decreases so that the values at 9° and 42° are nearly identical.

(To be continued.)

ON THE REACTIONS OF FERRIC SALTS
WITH SULPHOCYANIDES.

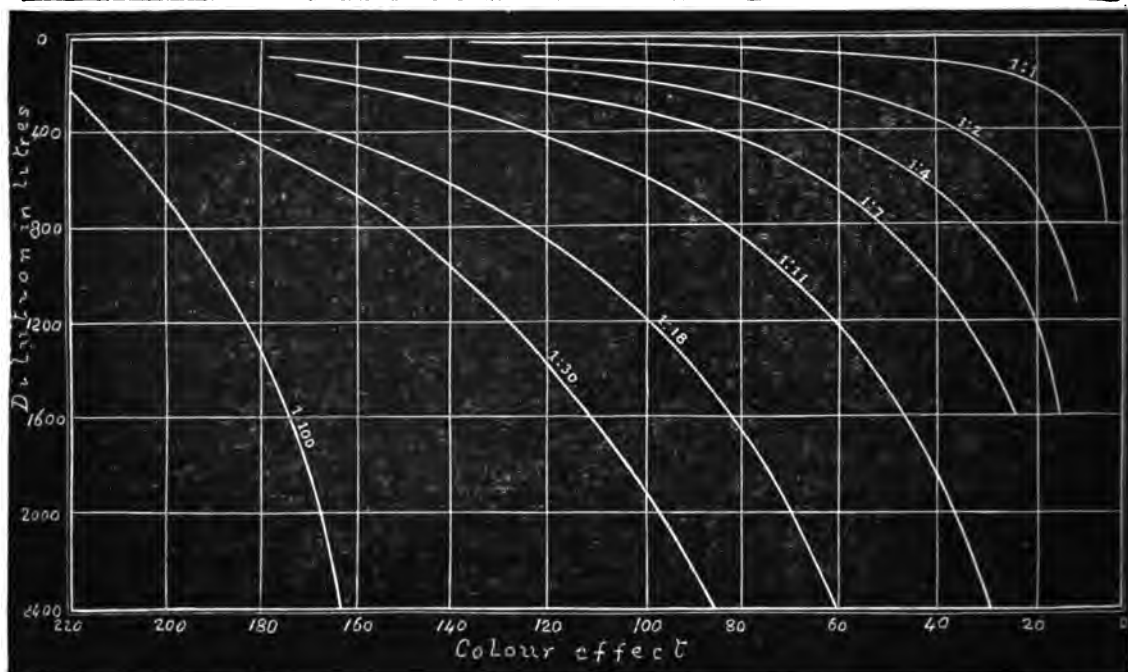
By H. M. VERNON, B.A.

THE colour reactions of various salts with one another were studied at considerable length by Gladstone (*Phil. Trans.*, 1855, 179), with a view to determining whether the quantity of a salt formed in a solution was dependent on the masses of the reacting salts in accordance with the law of mass action, the importance of which was then only beginning to be thoroughly recognised. The reactions of ferric salts with sulphocyanates were chiefly studied, the amount of ferric sulphocyanate formed being determined colorimetrically. The results obtained did not appear to obey the law of mass. As the correctness of the law of mass action has been thoroughly demonstrated by many chemists by numerous series of experiments, made under all possible variations of conditions, it would seem superfluous to bring forward any further proofs of its veracity. It is important, however, that all apparent exceptions to the law should be examined, and if possible adequate explanations for the variations be found, so that the law may be proved universally true, as it should be by theory. The object of this paper is, therefore, to examine the reactions of ferric salts and sulphocyanates under different conditions, so as to determine, if possible, the cause of the variations observed by Gladstone.

The colour comparisons were made in the same manner, and with the same apparatus, as those described by the writer in a paper on "The Dissociation of Electrolytes in Solution" (*CHEMICAL NEWS*, 1892, p. 105). All ferric sulphocyanate solutions were compared with a 0.1 per cent solution of the stain picric acid, which consists of a mixture of carmine and picric acid. This solution was of exactly the same tint as those of ferric sulphocyanate, and its use has several advantages over that of a standard solution containing ferric sulphocyanate. In the first place, it suffers no variation in colour with change of temperature, whilst ferric sulphocyanate solutions change considerably. It is not necessary, therefore, to bring this solution to a constant temperature when colour comparisons are made. Again, a ferric sulphocyanate solution does not remain a constant colour on keeping, but becomes lighter, owing to the decomposition of some of the ferric sulphocyanate and the deposition of small quantities of ferric oxide.

The method of determining the amount of ferric sulphocyanate formed differed essentially from that made use of by Gladstone, and indeed it is almost solely to his method that the variations observed by him are due. In the present experiments the solutions were compared by viewing them vertically in flat-bottomed tubes, and varying the thickness of the column of standard picric acid solution till of the same tint. In Gladstone's experiments the solutions were viewed horizontally through the sides of two test-glasses, one of which contained a standard solution and the other the solution to be compared. This solution was then diluted with water till of the same tint as the standard solution, and the amount of water so added taken as a measure of the increased amount of ferric sulphocyanate present in the solution. He assumed that the water added had no decomposing effect on the ferric sulphocyanate, and that, for instance, if of two solutions containing equal quantities of ferric sulphocyanate one was diluted to ten times its volume, it would still contain the same quantity of ferric sulphocyanate in solution, and that its tint, when viewed horizontally in a test-glass, would be exactly a tenth of its original value. This supposition was incorrect, as ferric sulphocyanate is very greatly affected by dilution. In the paper before referred to the writer showed that none of the salts examined, on dilution from 1 to 10 litres, decreased in colour more than about 30 per cent. Solutions of ferric sulphocyanate, in some cases,

Trichosanthe.—A. Tschirch (*Schweizer. Wochen-schrift Chem. Pharm. und Chemiker Zeitung*).—Trichosanthe is a green colouring-matter which the author has obtained from a Javanese fruit (*Trichosanthes pubera*). It is interesting as being the first green colouring-matter from the vegetable kingdom which differs decidedly from chlorophyll. The "thallochlor" which Berzelius obtained from the gonidia of *Cetraria islandica*, and which he regarded as a distinct vegetable colouring-matter, has been proved by Tschirch to be identical with chlorophyll.



show a colour decrease of nearly 90 per cent when rendered ten times more dilute.

The effects of dilution on solutions of ferric sulphocyanate were first of all examined fully with solutions containing, to 1 part of potassium sulphocyanate, 1, 2, 4, 7, 11, 18, 30, and 100 equivalents respectively, of ferric chloride. The colour value of a solution containing 1 c.c. of decinormal potassium sulphocyanate solution and 1 c.c. of equivalent decinormal ferric chloride solution diluted to 8 c.c., that is at a dilution of 80 litres, was taken as 50, and the other values were calculated against this. Measurements could not be made for more concentrated solutions than those of 40 litres dilution, as the tint of the solution was too dark. In most cases even 1 c.c. of decinormal KSCN to 100, 30, &c., equivalents of ferric chloride produced too deep a colour, so half this quantity had to be worked with. Solutions of several different strengths of all the salts used were prepared, so that the accuracy of the composition of the ferric sulphocyanate solutions might not be impaired by having to take too small volumes of the component solutions for correct measurement. All the solutions used were made up of equivalent strength, so that a normal solution of ferric chloride would only contain a sixth of its molecular weight, Fe_2Cl_6 , in grms., diluted to 1000 c.c. All the comparisons were made at 20° C. Most of the solutions were compared at about twenty different dilutions varying from 40 to 2400 litres. It was not possible to examine solutions containing only one or two equivalents of ferric chloride at a greater dilution than 800 litres, as the tint of the solution became too light, and also the colour alters somewhat from red to reddish yellow.

In the figure are given, diagrammatically, the colour values obtained for the different solutions. It will be seen that the more ferric chloride there is present in a solution, the more stable is the ferric sulphocyanate with regard to dilution. Even in the solution containing 100 equivalents the decrease of colour is considerable. Thus on dilution from 160 to 2400 litres the colour decreases from 222.8 to 162.6, or 27 per cent. With the 1:30 solution the colour decrease, for the same dilution, is over 60 per cent, and with the 1:18 solution about 73 per cent. In fact, it will be seen from the figure that the stability of

ferric sulphocyanate on dilution varies regularly with the amount of ferric chloride the solution contains. The 1:1 solution is therefore the most unstable of all, the colour decreasing about 94 per cent on dilution from 40 to 640 litres.

As was expected, the amount of ferric sulphocyanate formed in those solutions was found to vary with the amount of water present in accordance with the law of mass.

In the table are given the ratios for the value of the different solutions calculated on the formula—

$$\frac{1}{\theta} \times \frac{a}{A-a}$$

where θ is the concentration of the solution, A the colour value at infinite concentration, and a the colour value at the concentration θ . In accordance with the law of mass all the ratios calculated for each solution should be equal. At dilution A are given the numbers which were found by trial to agree best with the experimental values. These values must be taken as representing the true amounts of ferric sulphocyanate formed in the presence of varying quantities of ferric chloride, when no water is present to cause dissociation. They show that if no water were present, or if no dissociation took place, a solution containing ferric chloride and potassium sulphocyanate in equivalent proportions would contain twice as much ferric sulphocyanate as a solution containing 100 equivalents of ferric chloride. The action of ferric chloride on a solution containing ferric sulphocyanate is thus twofold. On the one hand, it exerts a decomposing action, it perhaps tending to form a basic salt, of less colour effect; whilst, on the other hand, it forms a solution which does not cause the dissociation of the ferric sulphocyanate to the same extent as pure water does; so in most cases, on its addition, the amount of ferric sulphocyanate formed increases. A very concentrated solution of ferric sulphocyanate would show a decrease in colour on the further addition of ferric chloride, and not an increase. If the curves in the figure are produced, it will be seen that at a dilution of 100 litres the colour values of the 30 and 18 equivalent solutions would be greater than that of the 100 equivalent solution.

Dilution in litres.	Proportion of Ferric Chloride to 1 part Potassium Sulphocyanate							
	100	30	18	11	7	4	2	1
A	230	240	250	255	303	365	400	450
40	—	—	—	—	—	—	—	0.118
80	—	—	—	—	—	—	0.452	0.125
120	—	—	—	—	1.85	0.853	0.456	0.125
160	59.2	17.1	10.02	4.14	1.98	0.876	0.474	0.119
200	57.5	16.6	10.07	4.24	2.00	0.871	0.467	0.118
240	60.5	16.0	9.63	4.38	1.98	0.923	0.427	0.116
280	56.5	16.7	9.18	4.62	2.01	0.997	0.494	0.115
320	57.5	15.8	9.08	4.56	2.00	0.995	0.479	0.101
360	59.2	16.3	9.00	4.50	1.97	0.993	0.496	0.102
400	58.8	16.7	9.26	4.51	1.93	0.991	0.473	0.101
480	61.3	16.3	10.06	4.69	1.93	0.986	0.441	0.096
560	60.5	15.6	10.03	4.83	1.98	0.978	0.448	0.092
640	60.0	14.7	9.04	4.77	2.04	0.955	0.493	0.092
720	52.5	14.9	9.60	4.48	2.01	0.939	0.435	—
800	57.1	14.7	9.27	4.82	2.01	0.910	0.402	—
960	54.0	16.4	10.10	4.73	2.02	0.902	0.401	—
1120	56.5	17.3	9.67	4.55	1.92	0.929	—	—
1280	60.7	17.1	9.89	4.63	1.81	0.936	—	—
1440	68.4	16.9	9.00	4.53	1.91	0.958	—	—
1600	54.9	16.7	9.79	4.39	1.90	0.954	—	—
1760	58.4	16.8	9.05	4.40	—	—	—	—
2080	67.0	16.4	10.11	4.11	—	—	—	—
2400	68.9	16.4	9.34	4.41	—	—	—	—

It is evident, therefore, that the law of mass plays a different part in the formation of ferric sulphocyanate from that accorded it by Gladstone, the increase of colour on the addition of excess of ferric chloride being merely due to the fact that the dissociation of the coloured salt is decreased to an extent great enough to overpower the effect due to the actual decomposition of the salt.

From the table it will be seen that the values for the decrease of colour effect on dilution obey the law of mass fairly regularly. The ratios for the 1:100 solution show greater variations than those for the other solutions, as the number calculated for A is but slightly larger than the experimental numbers obtained at other dilutions, and so a small error becomes considerably magnified. Thus an increase of 1 per cent in the colour value found at dilution 10 would cause the ratio in the table to increase from 59 to 67. The extreme ratios do not, in fact, indicate an error of more than about 2 per cent in any of the colorimetric measurements. This is as accurate as one can hope to make such determinations, and it is only after considerable practice that the eye can judge to within these limits. The solutions containing 30 and 18 equivalents of ferric chloride gave moderately regular values; but solutions containing 11, 7, 4, and 2 equivalents respectively, give values which are rather less for the small and great dilutions than for the moderate dilutions. This may perhaps be due to experimental error for the 11, 7, and 4 equivalent solutions, but it seems too large and well-marked to be put down to this cause in the case of the two equivalent solutions. What it can be due to is not known; but it must be remembered that the solutions do not contain merely ferric sulphocyanate in a more or less dissociated state, but also potassium chloride and undecomposed ferric chloride, and it is possible that the variations may be due to some secondary actions taking place between these salts. The solution containing equivalent quantities of ferric chloride and potassium sulphocyanate gives values which show a slight decrease as dilution proceeds. Whatever value for A the colour numbers are calculated against, it is found that the ratio values always showed a decrease for the more dilute solutions, the value 450 giving the least decrease. This value 450 must be taken as the colour the ferric sulphocyanate would show in a solution if it were unaffected by the presence of water or other salts, for in the equal equivalents solution at infinite concentration there can only be present potassium chloride besides the ferric

sulphocyanate, and it is not probable that this salt would have any decomposing effect. As therefore, at a dilution of 640 litres, the colour value is only 5.1, the solution only contains about a ninetieth part of the possible quantity of ferric sulphocyanate. That ferric chloride and potassium sulphocyanate, in equivalent quantities, react almost completely at infinite concentration to form ferric sulphocyanate, is proved by comparing their colour effect with that of a solution containing only ferric sulphocyanate. Such a solution was prepared by mixing equivalent quantities of barium sulphocyanate and ferric sulphate solutions, and allowing the precipitated barium sulphate to subside. This solution possessed a colour effect almost the same as that of a solution of equivalent quantities of ferric chloride and potassium sulphocyanate, and also it was affected to the same extent by dilution. Thus at a dilution of 40 litres the colour effect was 84.3; at 80 litres, 50.7; at 160 litres, 24.2; and at 400 litres, 8.7. The colour values of the ferric chloride and potassium sulphocyanate solution, at the same dilutions, are 86.0, 50.0, 25.3, and 8.9 respectively.

A similar series of determinations to the above was then made, in which the proportion of ferric chloride was kept constant, and that of the potassium sulphocyanate varied. It was thought that the values obtained would probably be of the same order as the previous series, but such did not prove to be the case. Solutions containing to one equivalent of ferric chloride 100, 30, 18, 11, 7, 4, 2, and 1 equivalents respectively of potassium sulphocyanate were examined at the same dilutions as the former series. As the numbers obtained do not serve as an illustration of the validity of the law of mass, in that they decrease at a greater rate than in proportion to the quantity of water added, they are not given here. The cause of this greater decrease was not discovered. It may have been due to a trace of impurity in the sodium sulphocyanate. So unstable is the coloured salt that the substitution of tap water for distilled water in a solution may decrease the colour effect by more than half.

(To be continued.)

THE SYNTHESIS OF SUGARS.*

By W. E. STONE, Purdue University.

(Continued from p. 166).

FISCHER's next step was to renew his studies upon one of the natural sugar bodies, *vis.*, mannit. This, as was already known, was converted by oxidation, first into the aldehyd, mannose, and then into the monobasic mannonic acid, $\text{CH}_2\text{OH}(\text{CHOH})_4\text{COOH}$. This acid, however, had not been well studied, owing to the difficulty of isolating it. Here again the versatile reagent, phenylhydrazine, came into play, producing with the acid, in mixture with impurities, a crystallisable "hydrazide" from which the pure acid was afterwards obtained as a lactone (*Berichte der Deutschen Chemischen Gesellschaft*, xxii., 2728, 3219).

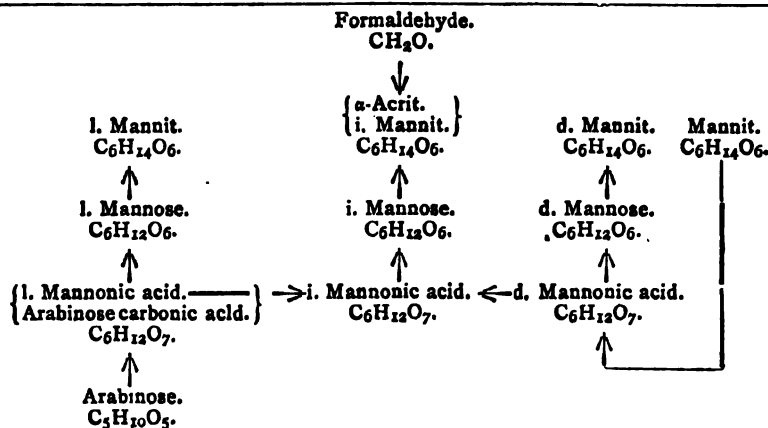
A wide gap in our understanding of the relations between different sugars was bridged when it was recognised that this mannonic acid lactone was isomeric with the arabinose-carbonic acid lactone already referred to. Here again appeared a remarkable difference in the optical properties of these isomers, which were otherwise practically identical. The mannose derivative was *dextro-rotatory*, and the arabinose derivative *levo-rotatory*. Moreover, when these optically opposed isomers were brought together in watery solution, in molecular proportions, they united to form a new lactone, like the others in all respects, save that it was *optically inactive* (*Berichte D. Ch. G.*, xxii., 370). This corresponds entirely with the well-known relation between the active and inactive modifications of tartaric acid.

* *Agricultural Science*, vi., No. 4.

Fischer now had in hand three related isomeric acids of the sugar group. His next step was to reduce them by sodium amalgam in acid solution to their corresponding aldehyds (*Berichte D. Ch. G.*, xxii., 2204, and xxiii., 930). In this way were obtained three isomeric aldehyd sugars, corresponding to the acids from which they were derived—one dextro-rotatory, one lævo-rotatory, and one inactive. These aldehyd sugars were further reduced to their corresponding hexatomic alcohols, retaining in each case their characteristic optical properties.

The significance of this optical series of isomers now became very great, since it strongly argued the possibility that all the natural sugars, previously known in only one form, might actually exist in optically opposed, or even inactive, isomeric forms, thus greatly increasing their possible number.

The completion of this series by the production of the inactive mannit led to the astonishing fact that it was identical with the α -acrit obtained synthetically from formaldehyd, and that here the synthetical and natural derivatives met. To distinguish between these dextro, lævo, and inactive isomers, Fischer adopted the prefixes d., l., and i., respectively. The following diagram will make the relation between these derivatives apparent (*Berichte D. Ch. G.*, xxiii., 2131.—Adapted).

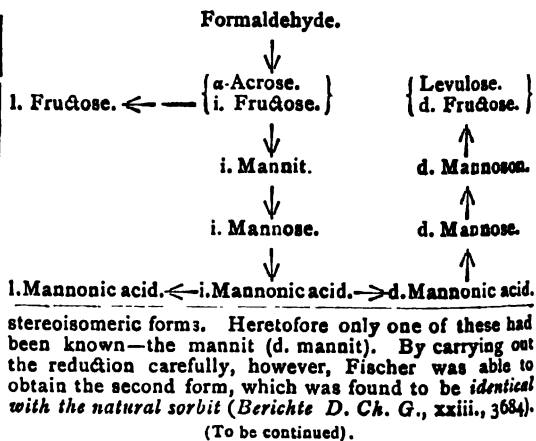


Mention has already been made of the separation of the α -acrose from its impurities as the α -acrosazon from which the sugar was regenerated. This α -acrose was optically inactive, but otherwise identical with levulose, or, as Fischer designates it, *fructose*. The synthetic α -acrose was, therefore, i. fructose (*Berichte D. Ch. G.*, xxiii., 384, 387). This completed, therefore, the synthesis of a regular member of one of the groups of sugars, although the product was not a body previously known. It remained now to show how the transition from the inactive synthetic product to one of the optically active natural sugars could be made. The i. mannonic acid had been prepared by combining the d. and l. mannonic acids. It now became Fischer's task to decompose an optically inactive body into its active components, or by destroying one to set free the other. For this purpose he made use of Pasteur's device of subjecting the synthetic i. fructose to fermentation, and found in fact that the yeast destroyed only one of its components, *viz.*, that which rotated to the left, leaving behind the dextro-rotatory member (*Berichte D. Ch. G.*, xxiii., 389). The yeast had acted upon the mixture in such a way as to remove the natural or lævo-fructose, rejecting its optical opposite. The latter, although dextro-rotatory, is classified by Fischer as l. fructose, while the natural fructose, although lævo-rotatory, is called by him d. fructose, for the purpose of bringing all the natural sugars into the "d." series, where indeed they all come naturally with the exception of fructose.

The last operation, while it yielded a new sugar, failed to close the gap between the synthetic and natural sugars, and recourse was again had to a new method (*Berichte D. Ch. G.*, xxiii., 389). Starting where the synthetical processes had ended, with the α -acrit, or i. mannit, this was converted by oxidation into i. mannonic acid. By preparing from this its strychnine salts, it was separated into the d. and l. mannonic acids, and these, by means of sodium amalgam, were reduced to the d. and l. mannose respectively. The d. mannose was converted into the d. mannosazon, and this in turn into the d. mannoson, which on reduction yielded, *not d. mannose, as might have been expected, but d. fructose*, identical with the natural fructose or levulose. This effected the complete synthesis of a natural sugar. The diagram below will illustrate the different steps of the operation.

On referring to the previous diagram, it will be seen that all the intervening stages between formaldehyd and the natural levulose and mannit had been taken, and in addition to this the heretofore entirely unknown and unsuspected inactive and lævo-modifications of these had been discovered.

By reduction of fructose to the corresponding hexatomic alcohol, the characteristic ketone group becomes asymmetrical, and the alcohol should theoretically have two



Borough Road Polytechnic Institute.—A class for the study of the Manufacture of Oils and Colours, and of Oils and Fats, commenced at the above Institute on Tuesday, Oct. 4. The class will be conducted by Mr. J. G. McIntosh, for whom a small laboratory has been specially fitted up to enable students to gain something more than mere book knowledge.

ON A FOSSIL WOOD CONTAINING FLUORINE.

By Dr. T. L. PHIPSON, F.C.S., &c.,
Graduate of the Faculties of Science and Medicine of the
University of Brussels.

WITH regard to the notes published recently in the *Comptes Rendus* of the Paris Academy of Sciences by Adolphe Carnot, and more particularly the one entitled "On the Composition of Fossil Bones and the Variation of the Amount of Fluorine contained in them in different Geological Strata," I wish to state that thirty years ago I made the analysis of a fossil wood from the Isle of Wight which yielded 32.45 per cent of phosphoric acid and 3.90 of fluorine. It had the following character:—Colour, brown; structure of wood, ductile; specific gravity = 2.71; locality, in the green sand (cretaceous) of the Isle of Wight. The specimen which found its way into my laboratory weighed over 4 lbs. The complete analysis showed that it had been fossilised by phosphate of lime and fluor-spar; had it been an ordinary mineral substance, it would have been looked upon probably as a mixture of apatite and fluor-spar. In spite of its enormous age, it contained 6.62 of organic matter. This organic matter might certainly have been due to infiltration, but the fossil *teredos* which I took with my own hands from the Brussels tertiary sands gave a distinct odour of the sea when the rock containing them was broken with the hammer.

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NEW METHODS FOR QUANTITATIVE ANALYSIS.*

By A. BAUMANN.

THE author proposes certain procedures in which use is made of hydrogen peroxide.

Concerning the decomposition which takes place on the action of chromic acid or a chromate upon hydrogen peroxide in presence of free acid, there have prevailed in part contradictory views. The exact knowledge of this reaction has obtained a higher significance for analytical chemistry since Carnot brought it into use for the determination of chromic acid. The same reaction has been further recommended for the determination of hydrogen peroxide, though A. H. Allen and G. Lunge have pointed out that the percentage of hydrogen peroxide in a solution cannot be accurately determined with chromic acid, as the reaction with an excess of chromic acid does not take place smoothly and completely.

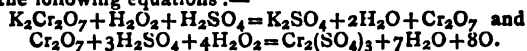
According to H. Aschoff, on the action of hydrogen peroxide upon an acid solution of potassium bichromate, so much oxygen is liberated that 8 atoms of oxygen go to 1 mol. of potassium bichromate.

On the other hand, Berthelot, who has closely studied the behaviour of hydrogen peroxide with chromic acid, finds that such a decomposition occurs only if the solution of chromic acid is allowed to flow slowly into the solution of the hydrogen peroxide. If we proceed inversely and pour the hydrogen peroxide gradually into the chromic acid only 6 atoms of oxygen are set at liberty.

According to the numerous experiments of Baumann and Lübcke the statements of Berthelot do not hold good on working with strongly diluted solutions in presence of an excess of sulphuric acid and mixing the reacting substances at once. On the contrary, Baumann and Lübcke confirm the results of Aschoff.

Hence the reaction between chromic acid and excess of hydrogen peroxide in largely diluted solutions mixed

with an excess of sulphuric acid take place according to the following equations:—



The chromic acid is therefore first converted into perchromic acid, which is then reduced by the hydrogen peroxide to chromium oxide, whereby half of the oxygen given off is derived from the hydrogen peroxide. After the manner of the decomposition of chromic acid has been placed beyond doubt for all cases which come under consideration in the methods to be described below, it has become possible to determine a greater number of substances by gas-analysis.

In these gas-volumetric determinations Baumann, as regards the apparatus to be employed, lays particular weight upon the point that both the gas burette and the generating vessel are under water. Hence he recommends as previously, in the valuation of manganese by the gas volumetric method, P. Wagner's azotometer. Baumann uses also a modification of Wagner's apparatus, distinguished by its simplicity. The author avoids the use of reduction instruments of any kind, as they complicate the analysis in a quite needless manner and still afford no absolute certainty for the correct calculation of the results. It seems most convenient to work out accurate special tables, and some such have been already calculated by Lübcke.

1. *Determination of Chromic Acid.*—The liquid containing the chromic acid, which must not be too concentrated, and should be in volume from 10 to 50 c.c., with 10 c.c. of dilute sulphuric acid (1:5), is placed in the wide space of the generating vessel. The small glass cylinder melted to it is charged with from 5 to 10 c.c. of commercial hydrogen peroxide. After the generating vessel has stood for ten to fifteen minutes in water of the temperature of the room, and the water stands at an equal height in both limbs of the U-tube of the measuring apparatus and reaches exactly 0 in the measuring tube, the hydrogen peroxide is poured into the solution of chromic acid.

Water is now allowed to flow out of the measuring apparatus, taking care that during the development of the gas the liquid stands rather lower in the tube which is not graduated. It is shaken round well, the cock over the generating vessel being kept closed during shaking and opened only for a short time, always after shaking for about half a minute, until the chief quantity of the oxygen has been liberated. Almost the entire quantity is set free in the first two minutes. In order to expel the rest (about 1 c.c.) powerful shaking is required for about five or six minutes. If no further increase of volume is perceptible in the measuring tube, the generating vessel is returned to the water-trough, and after the lapse of ten to fifteen minutes, and after the level of the water in the tubes of the measuring apparatus has been equalised, the volume of gas is read off.

This volume is reduced to 0°, and 760 m.m. of the barometer by a simple multiplication, according to Baumann's "Tables for Gasometry" (Munich: Reiger). If the number found is multiplied by 2.246 we find the weight of the chromic acid sought for (CrO_3 in m.grms.), as 1 c.c. of oxygen corresponds to 2.246 m.grms. CrO_3 ; or we may use the table of L. Vanino. We have then to multiply the volume of oxygen as read off with the number in the table, and then the product with 1.5716, as 1 m.grm. oxygen corresponds to 1.5716 m.grm. chromic acid. The results obtained by the author in this manner are very satisfactory.

The gas-volumetric determination of oxygen can also be effected with hydrochloric acid instead of sulphuric acid. The quantity of free hydrochloric acid for an experiment must not, however, exceed 4 c.c. of dilute hydrochloric acid (1:2) to 40 c.c. of the dilute solution of chromic acid, as otherwise errors may be occasioned by the liberation of chlorine, and more gases may be evolved than corresponds to the theoretical value.

* *Zeit. für Angew. Chemie* and *Zeit. für Analytische Chemie*.

The presence of nitric acid does not interfere if its quantity does not exceed 0.2 grm. in the solution examined. Larger quantities diminish the results, since only 7 to 7.5 atoms of oxygen are set free for each mol. of bichromate.

According to Lübcke the injurious influence of nitric and hydrochloric acid is diminished by the presence of free sulphuric acid. Acetic acid and succinic acid do not interfere with the reaction. Such organic substances as are readily oxidised by chromic acid (tartaric acid, oxalic acid, sugar, alcohol), prevent an accurate determination of chromic acid or render it quite impossible.

By means of the gas-volumetric determination of chromic acid it is possible in a convenient manner to find the standard of a solution of potassium bichromate without the aid of a balance or of other standard solutions. Here we have to consider that not all the oxygen evolved is derived from the chromic acid. Of the eight atoms of oxygen liberated from a molecule of bichromate only three are to be ascribed to the oxidation value of the solution of potassium bichromate.

The standard of such a solution is obtained by first multiplying the volume of gas given off with 0.375, and then re-calculating the volume into weight by the aid of Vanino's table.

(To be continued).

DETERMINATIONS OF TANNIN ACCORDING TO GANTLER'S PROCESS.

A. KLINGER and A. Bujard come to the same conclusions as von Schröder and Pässler. The authors on their part confirm the statement that the consumption of permanganate by tanniferous solutions after the tannin has been precipitated with hide-powder cannot by any means be neglected, as Gantler asserts. If the filtrate from hide is neglected, in case of oak bark, they obtained 5 per cent of tannin in excess. As the hide-powder used generally contains soluble organic substances, its consumption of permanganate must be determined and subtracted.

As regards the objections of Procter, the authors found that certainly, as he alleges, an increased addition of sulphuric acid involves an increased consumption of permanganate, but only up to a certain limit. Klinger and Bujard used, according to Gantler's directions, 10 c.c. of sulphuric acid (1:5). On the addition of 20, 25, and 30 c.c. of sulphuric acid, A. Baier found the proportion of tannin increased by 2 per cent; a further increase of the addition (40 and 50 c.c.) had no perceptible influence on the last result.

In opposition to Procter's observation, that in one and the same extract of bark the consumption of permanganate varies as much as 2.2 c.c., the authors have always obtained results which agreed very well with each other.

The objection of Procter that any gelatinous constituents of the hide-powder had a great influence on titrating according to Gantler, whilst on titrating according to Löwenthal this is not the case, was found by the authors to be verified; but if, as they propose, a blank experiment is first made with hide-powder, this circumstance does not occasion an error.

The authors have by opportunity of these experiments determined the proportion of tannin in a new tannin material. It is the root of canaigre (*Rumex hymenosepalus*), a plant growing in Lower California, and much used in Texas for tannin. In the root, when dried at 100°, the authors found tannin:—

According to Löwenthal	33.62
„ Gantler	42.14
„ the gravimetric method .. .	40.80

—*Zeit. für Analytische Chemie.*

THE ACTION OF BARIUM PEROXIDE UPON METALLIC SALTS.

By W. KWASNIK.

NOT merely potassium ferricyanide, but a large number of other salts, act upon barium peroxide so as to liberate oxygen. The salts of the alkalies and alkaline earths do not liberate oxygen. Salts of magnesium act in this manner very slightly, and those of zinc and cadmium but little. Salts of nickel and cobalt occasion a vigorous development of gas, as do also the salts of iron, manganese, chrome, and aluminium. The hydroxides of the respective metals are formed, and half the oxygen present in the barium peroxide is set free. In the lower salts of the latter group the reaction takes place in two phases. An oxidation firstly takes place, and afterwards gaseous oxygen is liberated.

Cupric salts produce at once a brisk escape of oxygen.

By the salts of mercury, silver, and gold for each molecule of barium peroxide 2 atoms of oxygen are set free and the metallic salts are reduced. Platinum forms an exception from the behaviour of the precious metals just mentioned. If platinum chloride is used there is formed a soluble compound analogous to potassium platinum chloride. The double chlorides of platinum and an alkaline or alkaline earthy metal do not act upon barium peroxide. Platinum chloride (PtCl_4) and argento-platinum chloride (2AgCl.PtCl_4) are decomposed with separation of platinum or platinum and silver.

Barium peroxide yields oxygen not merely with soluble metallic compounds, but with such as are insoluble, although in the latter case the development is much slower. In many compounds the application of heat is necessary.—*Zeit. für Analytische Chemie.*

SEPARATION OF IRON FROM THE ELEMENTS BY A NEW PROCESS.

By J. W. ROTHE.

THE process is founded on the fact that all ferric salts, on repeated shaking out with ether in a hydrochloric solution at a proper concentration of the hydrochloric acid, give off all their iron to the ether in the form of ferric chloride.

Ferrous salts, under similar conditions, are not extracted by ether.

Manganous, nickelous salts, as well as the salts of chrome and aluminium, if shaken up in a similar manner do not yield any compounds soluble in ether.

Cobaltous and cupric salts are dissolved in variable quantities by ether, according to the respective proportions of these salts in the hydrochloric solutions; but the quantity of cobalt and copper dissolved is relatively very trifling. If the ethereal iron solution is then shaken up with hydrochloric acid solution of specific gravity 1.104, these slight impurities of cobalt and copper may be removed. Slight proportions of ferric chloride may certainly pass again into the hydrochloric solution and must be removed by again shaking out with ether.

In the application of this method to the examination of steel and iron certain conditions have to be observed, for which the following procedure has been found practicable. We dissolve 5 grms. of the sample in about 40 c.c. hydrochloric acid of specific gravity 1.124 (at 19° C.), placing the vessel upon the water-bath at a moderate heat. The solution is then evaporated to dryness at first on the water-bath and then in an air-bath at 120°. The dry residue is then covered with about 20 c.c. of the same hydrochloric acid, heated to boiling, and filtered off from the silica after dilution with a three-fold volume of hot water. The iron solution is concentrated in a porcelain capsule until vapours of hydrochloric acid escape, mixed with about 10 c.c. of concentrated hydrochloric acid, and

oxidised at the temperature of ebullition by means of from 2 to 2.5 c.c. nitric acid of specific gravity 1.4, added drop by drop. Finally the liquid is evaporated down to the consistence of a syrup or until a basic ferric chloride separates out. The solution thus prepared, about 10 c.c. is put in an apparatus of special construction, filled up to the volume of from 55–60 c.c. with hydrochloric acid of 1.124 (at 19°), and shaken out twice with ether. If relatively much copper and cobalt dissolve, both the first and the second ethereal solution of ferric chloride must be shaken out, each with 10 c.c. of hydrochloric acid of specific gravity 1.104, in order to remove the traces of copper and cobalt which have been dissolved in the ether along with the ferric chloride.

In preparing aluminiferous solutions of iron for shaking out with ether, particular care should be taken that the hydrochloric solution when concentrated is perfectly clear and contains no deposits of basic aluminium salts.—*Mitth. a. d. kgl. Techn. Versuchs Anstalten. Berlin* and *Chemiker Zeitung*.

ACTION OF SULPHUR IN PRESENCE OF WATER UPON THE SALTS FORMED BY THE POLYBASIC ACIDS.*

By J. B. SENDERENS.

I HAVE previously made known to the Society the results yielded by the action of sulphur in the presence of water upon the oxides of the salts formed by monobasic acids. Before explaining my new researches, I will make a slight correction concerning the oxides of nickel and cobalt. In the first moments of ebullition there are formed in both cases a sulphate and a hyposulphite, but as the operation continues, the hyposulphite gradually diminishes, in consequence of its formation into sulphate, so that at the end of the reaction the latter salt predominates exclusively in the liquid.

After this explanation, I come to the action of sulphur in presence of water upon the salts formed by the polybasic acids. Coloured reagents, and especially colorimetric observations, have shown us that the multiple acid functions superposed in the molecule of a polybasic acid may be—

(1) All strong; (2) all weak; (3) some strong and others moderate or weak.

1. Acids, the Acid Functions of which are Strong.

We consider as such the sulphuric, oxalic, and tartaric acids (bibasic); and the citric acid (tribasic).

Sulphur is without action upon the alkaline sulphates and oxalates in boiling solutions (whether acid or neutral), but it slightly decomposes the bibasic tartrate and the tribasic citrate, bringing their solutions to perfect neutrality. At the outset they have a slightly alkaline reaction with litmus and phenolphthalein.

Thus the action of sulphur upon the saline solutions in question indicates sulphuric, oxalic, and citric acids as having two strong acid functions. The same action attributes to tartaric acid a strong acid function and a medium acid function; and to citric acid two strong acid functions and a medium acid function.

2. Acids which have exclusively Weak Acid Functions.

Such are the carbonic and the boric acids. I have said in a previous communication that the solutions of the alkaline carbonates, whether neutral or acid, are completely decomposed by sulphur at the temperature of ebullition.

It is the same with the alkaline borates, acid and neutral. The analogy between these two kinds of salts extends to their metallic compounds. Thus the copper,

nickel, and lead borates are readily reduced by sulphur in presence of boiling water, as are also the corresponding carbonates. Boric acid is set free and the sulphur forms a sulphide and a sulphate with the bases.

3. Acids, the Acid Functions of which are some of them Strong and others Weak.

This case is presented by ortho-phosphoric acid, PO_4H_3 .

(a). *Alkaline Phosphates*.—M. Filhol and I have shown long ago that sulphur easily seizes in heat the third molecule of soda, yielding a polysulphide and a thiosulphate. I have since observed that there is an escape of sulphuretted hydrogen from the destruction of the polysulphide. The reaction does not stop at the disodium phosphate, and on continuing the operation the latter salt gives up to the sulphur half a molecule of soda.

(B). *Alkaline earthy Phosphates*.—The barium and calcium phosphates are decomposed by sulphur in presence of boiling water. Hydrogen sulphide escapes, and the liquid contains thiosulphate. This decomposition is extremely slow and does not go beyond the third molecule of the base. If we boil water with sulphur and the monoacid or diacid alkaline-earthly phosphates, the latter salts do not undergo any change.

It results from these experiments that phosphoric acid with potassa or soda behaves like an acid possessing 1.5 of a strong acid function, but the baryta and lime as having 2 strong acid functions and 1 of a medium acid. Sulphur, in fact, which has no action upon sodium or barium sulphate has as little action upon sesquisodium phosphate or di-barium phosphate, whilst it decomposes the alkaline and alkaline-earthly carbonates and acetates to which it has been sought to assimilate the phosphate as far as the second molecule of the base is concerned.

The action of sulphur upon the metallic phosphates in presence of water shows us that the ortho-phosphoric acid has three strong acid functions.

(γ). *Metallic Phosphates*.—The tribasic silver phosphates, like the dibasic salt, are completely reduced by sulphur in presence of boiling water, according to the equation—



The three copper phosphates, $(\text{PO}_4)_2\text{Cu}_3$, $(\text{PO}_4)\text{HCu}$, $(\text{PO}_4)_2\text{H}_2\text{Cu}$, are likewise decomposed with the same reactions as the silver salts.

The lead, nickel, and cobalt phosphates remained unaffected in presence of sulphur and boiling water.

Thus, with reference to the metallic oxides, phosphoric acid possesses three strong acid functions, just as sulphuric acid has two with reference to the same oxides. In fact, copper and silver sulphates are reduced by sulphur in presence of water, as are also the phosphates of the same metals; but the tribasic phosphates of lead, nickel, and cobalt resist the action of sulphur like the corresponding sulphates.

(To be continued.)

NOTICES OF BOOKS.

Matriculation Chemistry: Chemistry of the Non-Metallic Elements and their Compounds. By TEMPLE ORME. London: Lawrence and Bullen. 1892. 12mo., pp. 240.

THIS little book raises anew the painful question—By what process do the authors of such treatises persuade themselves that there is still need for chemical manuals "intended for beginners"?

We see nothing objectionable in the work before us, but as little can we discover its *raison d'être*. Surely, pending some capital discovery, such as the decomposition of one of the reputed elements, beginners might find

* *Bulletin de la Soc. Chimique.*

their wants met by some one of the multitude of existing treatises.

The Practical Polish and Varnish Maker. A Treatise containing 750 Practical Receipts and Formulæ for the Manufacture of Polishes, Lacquers, Varnishes, and Japans of all Kinds, for Workers in Wood and Metal, and Directions for Using. By H. C. STANDAGE (Author of "The Artists' Manual of Pigments," &c.). London: E. and F. Spon. New York: Spon and Chamberlain. Small 8vo., pp. 260.

THIS book consists almost entirely of recipes, the value of which can only be decided on by actual use. The author informs us that many of the formulæ given have been practically tested by him, and that the sources from which his information has been drawn are perfectly trustworthy. He states the precise proportions of the ingredients to be used, and gives full instructions on the manner of putting them together. Practical directions have also been given for the use of the various varnishes, polishes, &c.

As the work is intended mainly for amateurs, it treats of the so-called spirit varnishes alone. The oil varnishes have not been included in the author's plan, as their preparation requires special and costly appliances.

The first chapter of the book gives an account of the materials used in making up varnishes; then follow directions for filtering and bleaching varnishes and lacquers, and the remainder of the book is devoted to practical recipes.

The book, so far as we can judge, seems calculated to be very useful.

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—I observe in the *CHEMICAL NEWS* (p. 172) a letter from Mr. G. H. Robertson, Registrar of the Institute of Chemistry. Kindly permit me to make a few observations upon the action of the Institute in the case he has mentioned.

A certain appointment was vacant, legally and morally, for which I made application in writing. In the course of a few days, I received from Mr. Groves, then Secretary, a letter stating that a Fellow of the Institute had lodged a complaint with the Censors against me of unprofessional conduct, which, as stated by the Censors, consisted in "that I had applied for an appointment which another Fellow held." I never applied for any appointment held by any Fellow; I have never applied for any appointment that was not legally vacant, and the appointment I did apply for was legally filled up some months afterwards. The Council, taking advantage of the powers contained in their Charter, and acting under the influence of Teutonic terror, removed my name from the Register upon an absolutely false charge for an offence I did not commit.

The action against the Institute was raised so as to enable me to obtain possession of the contents of a libellous letter written to the President, and it must become apparent to the novice that a "body corporate," possessed of practically unlimited powers over the actions of its members, must have sinned grievously and been hard pressed when they agreed to pay their own costs—costs amounting to about £500—if I withdrew the case. They do not stop there; but they go further, and express through a most eminent Q. C. "that they have no charge against my professional capabilities or personal character, but of the view of the Council on the professional conduct of the plaintiff on one occasion." That one occasion is

the charge stated above, and I utterly defy them to substantiate or repeat this false charge, under cover of which my name was removed from the Register.

If my public and private character merits such high merit as they have acknowledged they do, Emeritus Fellow will in the future distinguish between past and present Fellows who still hold Certificates of Membership, although their names do not appear upon their Register. All things must have a beginning, as the Institute had. It is a young Society at variance with itself, and their actions have created the title of Emeritus Fellow.—I am &c.,

WILLIAM JOHNSTONE,
Emeritus Fellow of the Institute
of Chemistry.

London, October 4, 1892.

METHODS FOR THE DETERMINATION OF ORGANIC MATTER IN DRINKING WATER.

To the Editor of the Chemical News.

SIR,—In view of the very strongly worded assertions of articles on this subject which have recently appeared in the *CHEMICAL NEWS* (vol. lxvi., pp. 102 and 111), it may be allowable to direct attention to an extensive report which I prepared several years ago for the U.S. National Board of Health, giving the results of a careful study of the chief methods in use, and numerous analyses in which these methods were tested by simultaneous application under similar conditions to carefully selected samples of water of known character—some good and wholesome; some held, on good medical authority, to have actually produced disease; some artificially polluted with known forms of manufacturing refuse and products of disease—the history of each sample being in every case unknown to the analyst, and the sole object being an absolutely fair and impartial contrast between the methods employed.

The original paper forms a part of the Annual Report of the U.S. National Board of Health for 1882 to the Secretary of the Treasury, pp. 189 to 353, with tables; and an abstract, or, rather, a preliminary report, appeared in the *CHEMICAL NEWS* (vol. xlv., pp. 63, 72, 90, 101, 108; and vol. xlvii., pp. 218 and 232).—I am, &c.,

J. W. MALLET.

ON THE ORGANISATION OF SCIENCE.

To the Editor of the Chemical News.

SIR,—I am exceedingly sorry that in speaking of the very timely pamphlet by "A Free Lance" I did not express myself in a manner incapable of being misunderstood. I referred, of course, to what I and not a few others regard as the main defect of the Provincial Societies, viz., the unhappy attempt to combine the cultivation of science and of literature in one and the same organisation. The consequence is that literature obtains the lion's share, both of time at the Society's meetings, and of space in the printed Transactions. Science is even at times grossly insulted.—I am, &c.,

YOUR REVIEWER.

"Anicol."—F. Goldmann.—Under this name a "proprietary article" has been introduced to the world as the "sovereignest thing" for febrile affections. It has been unmasked, and is found to consist of 75 per cent antifebrine, 17.5 per cent sodium bicarbonate, and 7.5 per cent tartaric acid! It is modestly offered at about six times the price of antifebrine.—*Chemiker Zeitung* and *Pharm. Rundschau*.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 12, September 19, 1892.

The Action of Bromine in Presence of Aluminium Bromide upon Carbides with Cyclic Chains.—W. Markownikoff.—The author proposes the following rule. The action of bromine upon the naphthenes in presence of aluminium bromide at the ordinary temperature bears principally upon the atoms of hydrogen of the cyclic chain, transforming it into a benzene nucleus in which all the atoms of hydrogen are replaced by bromine whilst the lateral chains remain intact. But the most simple naphthene, hexahydrobenzene, C_6H_{12} , presents a remarkable exception, since it does not yield hexabromobenzene but another bromine product.

The Rotatory Power of Fibroine.—Leo Vignon.—The substance-precipitated from hydrochloric solutions of fibroine by alcohol has the same power of absorbing colouring-matters as ungummed silk.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 13.

Preparation and Purification of the Propylamines.—F. Chancel.—We may easily prepare the three propylamines by the action of aqueous ammonia upon propyl chloride if we take sufficient alcohol to dissolve the whole. The dry bases may be accurately separated by successive rectifications, and to complete their purification we isolate the primary base in the state of dipropyl-oxamide or of acid oxalate, the secondary base in the state of an acid oxalate, and the tertiary base as a picrate.

The Action of Oxalic Ether upon Aqueous Monopropylamine. Monopropyl-oxamic Acid.—F. Chancel.—Monopropyl-oxamic acid has the composition expressed by the formula $C_3H_7NO_2$. The author has obtained and examined its calcium and barium salts.

Propylamidoacetic Acid.—F. Chancel.—This compound is obtained by the action of monopropylamine upon ethylbromacetate. Its composition is $C_6H_{14}NO_2$. The author describes its hydrochlorate, its platino-chlorate ($C_3H_{12}NO_2 \cdot PtCl_6 + H_2O$), its chloraurate, and the copper propylamidoacetate.

Dibromogalllic Acid and the Dibromogallates.—Alex. Biatrix.—This acid ($C_6Br_2(OH)_3COOH$), forms white or slightly yellowish needles, sparingly soluble in cold water, very soluble in boiling water, alcohol, and ether. It takes a rose-colour in contact with alkalis; the ethereal solution takes an indigo-blue colour with baryta-water, which turns red on the addition of water. The author has prepared and determined the ammonium, sodium, zinc, lead, barium, quinine, and strychnine dibromogallates.

Researches on Persulphuric Acid and its Salts.—M. Berthelot.—The author has studied these bodies chiefly from a thermo-chemical point of view, determining the solution, neutralisation, and formation-heats.

Formation-Heat of Hydrazine and of Azothydric Acid.—This paper consists of a series of thermochemical determinations.

The Combustion- and Formation-Heats of Alcohol and of Formic and Acetic Acids.—MM. Berthelot and Matignon.—The character of this paper appears from the title.

Combustion- and Formation-Heats of the Nitrobenzenes.—MM. Berthelot and Matignon.—A thermo-

chemical study of dinitrobenzene in its ortho, meta, and para types; and of trinitrobenzene, symmetric and dissymmetric.

Thermo-chemical Data.—MM. Berthelot and Matignon.—Determination of the solution-heat of hydroxylamine, and of the neutralisation-heat of hippuric acid.

A Contribution to the History of the Mechanical Arts and of Artillery towards the End of the Middle Ages.—M. Berthelot.—Mention of a memoir published by M. Berthelot in the December number of the *Annales de Chimie et de Physique*.

New Method of Organic Analysis.—M. Berthelot.—The method consists in burning the compound in the calorimetric bomb in oxygen compressed at twenty-five atmospheres. The combustion is total and instantaneous. The sulphur in organic matters may be completely determined by adding beforehand 10 c.c. of water. The sulphur remains in the water in the form of sulphuric acid. Phosphorus may be determined in a similar manner. Chlorine may also be determined by introducing previously into the bomb an aqueous solution of arsenious acid. For compounds very rich in chlorine the combustion is effected with the addition of a suitable dose of camphor.

On Nickel-Carbonyl.—M. Berthelot.—Carbon monoxide has the property of combining in the cold with nickel, forming special compounds analogous to the compound metallic radicles. Carbon monoxide behaves in this respect like the hydrocarbons.

Oxidation of Nickel-Carbonyl.—M. Berthelot.—The product of the analysis of the slow oxidation of this compound is whitish in small quantities, but it appears green in masses. Its composition is $C_2O_3Ni_3 \cdot 10H_2O$. It is the oxide of a complex radicle analogous to the croconic and rhodozenic acid.

On Ferro-Carbonyl.—M. Berthelot.—In order to combine with carbon monoxide the iron should be reduced with hydrogen slowly and at the lowest possible temperature, then washed and carefully dried. The reaction of carbon monoxide upon iron in this state takes place at about 45°. The combination of iron with carbon monoxide plays doubtless a part in certain reactions observed in metallurgy, such as the precipitation of the carbon of carbon monoxide in contact with iron (observed by Gruner), the formation of gaseous bubbles in softened iron (observed by Cailletet), &c.

Some New Observations on the Determination of Sulphur in Vegetable Soil, and the Nature of the Compounds which it Forms.—MM. Berthelot and Matignon.—Sulphur exists in vegetable soils and in plants in the state of special organic principles, the proportion of which often far exceeds that of the sulphates also present. The organic compounds contained in the soil are very stable.

Silica in Plants.—M. Berthelot and G. André.—The authors trace the presence of silica in wheat at different stages of its growth.

Researches on the Humic Substances.—M. Berthelot and G. André.—Humic anhydride shows at once the properties of the acid anhydrides and the alcoholic anhydrides, and is comparable to the lactones.

Calorimetric Researches on Humic Acid derived from Sugar.—MM. Berthelot and André.—Humic acid is a polybasic acid capable of losing a part of its water of hydration by simple desiccation, and even in water at the ordinary temperature by reason of a true dissociation.

The Spontaneous Oxidation of Humic Acid and Vegetable Mould.—M. Berthelot and G. André.—Already inserted.

The Fermentation of Blood.—M. Berthelot and G. André.—The products of the fermentation are carbonic acid, free from hydrogen and nitrogen, ammonia, volatile fatty acids, fixed nitrogenous principles,

MISCELLANEOUS.

Specific Determination of Xylose.—G. Bertrand.—If there is only a very small quantity of xylose available, e.g., 0.1 grm., its nature may be determined by proceeding as follows. The sample, supposed to be crude syrup of xylose, is left to itself. If crystallisation is slow in appearing the syrup, with the aid of heat, is stirred up in absolute alcohol. After sufficient settling the cold alcoholic solution is decanted off to separate it from the deposit formed and evaporated to a syrupy consistence; the crystallisation is then almost always easy. The crystals are then examined and drained in a porous plate. They are then stirred up in alcohol and drained anew, repeating this operation if needful. It is now necessary to ascertain if we have to do with xylose. For this purpose we heat a few m.grms. with a little hydrochloric acid and a trace of orcin. If the mixture takes a violet-blue colour we are in presence of a pentose, but if the colour is a reddish-orange we have one of the glycoses in C₆. It is only necessary to distinguish xylose from arabinose by means of cadmium xylono-bromide.—*Bull. Soc. Chim. de Paris*, Series 3, No. 14.

The Swiss Scientific Association.—The seventy-fifth Congress of this body took place at Bâle from September 4th to 7th. Prof. Forel discussed the "Thermics" of lakes, with especial reference to the lake of Geneva. He considers lakes as storehouses of heat, and consequently of the highest physical and biological importance. Prof. C. Schmid discoursed on the metamorphosis of the Alpine rocks, exhibiting splendid thin slides of different rocks prepared in polarised light. Prof. Noelting communicated the results which he had recently obtained whilst prosecuting his researches on the triphenylmethane colouring-matters. Goldschmidt read a paper on the aldoximes, and Schar treated on the influence of hydrocyanic acid upon certain ferments, and on the poisonous principle of the seeds of *Abrus precatorius*. Wislicenus discussed the conversion of fumaric acid into maleic acid in presence of hydrochloric acid. A communication by Professor Thiescher on the chemistry of the spermatozoa excited no small sensation. Prof. Raoul Pidet delivered an address to the Association on the part of low temperatures in contemporary Science. He showed that at extremely low temperatures the reactions of bodies, generally known as "affinity," came to an end. The Association will meet next year at Lausanne.—*Chemiker Zeitung*.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Monazite.—We will be greatly obliged for the name of any technical or scientific books giving information about monazite, where it is found, and for what use it is employed.—RICHARD BAKER, SON, AND CO.

Detection of Oils.—Would any correspondent be kind enough to inform me how to separate, or at least detect, castor oil, rape seed oil, cotton seed oil, olive oil, linseed oil, from or in a paste containing vaseline; and each of the above oils in succession (1) in their simple form, (2) when they are saponified.—X. Y. Z.

LECTURER ON ORGANIC CHEMISTRY.

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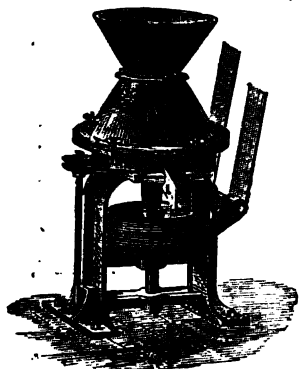
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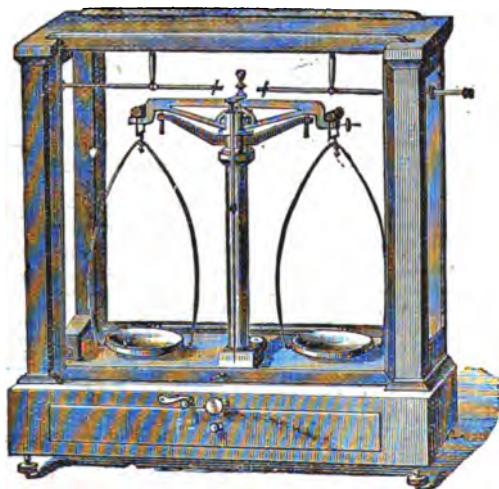


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VOL. LXVI., No. 1716.

NOTE ON THE CAUSE OF THE COLOUR OF MILK.

By SIR CHARLES A. CAMERON.

IN the third volume (recently published) of the new edition of Watts' "Dictionary of Chemistry," the subject of the constitution of milk globules is discussed at some length. There are several authorities quoted in opposition to Henle's statement that the fat globules have albuminous envelopes. I would like to state that before any of the authorities quoted had contravened Henle's statement I had pointed out in a paper (*Scientific Proceedings of the Royal Dublin Society*, 1875), read before the Royal Dublin Society, 18th January, 1875, that free fat globules were exceedingly numerous in milk. I also stated that the colour of milk was due to the large number of casein films suspended in it, and not to an emulsion of fats and albumenoids.

I succeeded in extracting from milk all its fats save a mere trace, and yet the former remained a perfectly white opaque fluid. Butter-milk, which contains from 0.3 to 0.6 per cent of fats only, is whiter than milk diluted with its own weight of water, yet the latter is three times as rich in fats.

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By WILLIAM HAMLET, F.I.C.,
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To the left of the front is an upright frame made to hold a sheet of glass six inches square; into the groove made in the frame, ruby, violet, green, and colourless glasses may be inserted as wanted. At a point two inches from the left edge is a brass rod six inches high which serves to hold a glass tube bearing a fine platinum wire for flame reactions.

The lamp may be any one of the many varieties of paraffin or grease lamps having a flat wick. In my own case I employ the lamp found in Letcher's blowpipe outfit, using solid paraffin as fuel. On the extreme left, just midway across the board, is a brass plate 2×1 inches, hard soldered on to a universal joint (not shown in the photograph, because I at first used merely a slip of wood hinged to a block). This forms a convenient support when protected by a piece of asbestos millboard for charcoal pellets or cubes, as well as for plaster slabs and aluminium plates. The upright prism of porcelain is used for cupelling.

On the right is embedded into the table a flat steel anvil and an agate mortar. Such a blowpipe becomes a valuable adjunct to the laboratory equipment, and instead of the blowpipe being despised and consigned to the drawer or box of odds and ends it finds a useful place on the working bench. With such a piece of apparatus one can get a very clearly defined reduction or oxidation flame, and when the jet slopes down on to the wick at the proper angle, it is easy to produce a flame four inches long and so steady that I have actually cupelled off a lead button as perfectly as it could have been done in the muffle. Such a thing is sometimes stated in books, but I never saw it accomplished until I actually did it myself with the apparatus I now describe.

Using the flame colouration and a blue screen, it is quite possible to see the potassium flame amid the abundance of sodium salts in urine. Conversely, the presence of sodium salts in potassium compounds may be recognised by using the green tinted screen.

Altogether it is the most efficient and the most easily handled blowpipe arrangement I know of, and I made good use of it during my recent visit to the Broken Hill Silver Lead Mines.

With the steady flame obtained, Von Kobell's reaction for bismuth compounds gives most brilliant results on a slab of plaster of Paris, and with dry thiosulphate all the reactions may be instantly obtained in the dry way that are usually given in the wet way with sulphuretted hydrogen.

THE ANALYSIS OF THE CAVENDISH BANANA (*MUSCA CAVENDISHII*) IN RELATION TO ITS VALUE AS A FOOD.*

By W. M. DOHERTY,
Assistant Government Analyst, New South Wales.

THE value of the banana as a perfect food has been frequently extolled, but so far as I can learn no analysis of the fruit has yet been published, and nothing is known of its food value beyond general practical experience. To supply a conspicuous gap on the list of fruits which have been submitted to investigation this analysis has been undertaken.

The Cavendish, or, as it is sometimes called, Fiji variety, has been selected because of its enormous consumption in Australia, where it has almost completely dislodged all the other kinds. This banana is the product of a plant which grows only to a height of about six feet, and it has therefore received the appellation "dwarf." Its original home was China, from which country it was brought to England by the Duke of Devonshire (hence the name Cavendish), and cultivated by him in the celebrated Chatsworth Gardens. From England it was brought to Fiji by a party of missionaries, thence finding its way to Australia. It is now grown to a considerable extent in Queensland, and will thrive well in the northern parts of New South Wales, especially in the Tweed River district.

The banana has been described as "the produce of one of the most splendid plants of the world. Underground there is a substantial root stock of long duration, from which rise stems, branchless, like those of palms, and carrying upon the summit half a dozen superb leaves of great size, of a rich lucid green, and which arch away from it on their long petioles, magnificently. The veining of the leaves is of a very rare and elegant kind, which has been fittingly called featherlike; innumerable lateral veins flowing from the midrib in a curvilinear manner towards the margin. The stem is composed in reality of no more than the sheathing and closely compacted bases of the older petioles, in the heart of which, near the

* Exhibited before the Royal Society, N.S.W.

* Australasian Association for the Advancement of Science, Hobart, 1892, Section B.

ground, the flower bud is generated. This in due time develops itself from among the youngest leaves as a huge pendulous raceme, constituted of crimson bracts, which protect innumerable though rather trifling flowers, followed again in due time by the well-known fruits—cylindrical, six or eight inches long, an inch or more in diameter, slightly curved, and when ripe pale yellow. The clusters of fruit are often four feet long, and weigh from twelve to sixty or eighty pounds. In the tropics it is said that two plants will grow anywhere—the castor oil and the banana. This is not only true, but it may be added with equal justice that no plant furnishes man spontaneously with supplies so vast of a pleasant and nourishing food. In countries where the mean heat of the year is never lower than 75° F. the banana is the bread of the poor, and this all the year round, literally yielding fruit every month."

The analysis was made upon picked specimens, divested of the skin.

Composition in 100 Parts.

Water	75.71
Albumenoids	1.71
Starch	5.90
Sugar	3.00
Carbonaceous matter (non-nitrogenous) ..	11.24
Woody fibre	1.74
Ash	0.71

Composition of the Ash.

Potash (K ₂ O)	55.10
Soda (Na ₂ O)	12.00
Lime (CaO)	1.61
Magnesia (MgO)	5.41
Phosphoric acid (P ₂ O ₅)	7.70
Sulphuric acid (SO ₃)	1.80
Carbonic acid (CO ₂)	12.00
Chlorine (Cl)	1.10
Oxide of iron (Fe ₂ O ₃)	0.48
Silica (SiO ₂)	1.96
Oxide of manganese (MnO ₂)	0.15
Loss, &c.	0.69

100.00

Composition of the fruit, and percentage of mineral constituents, calculated dry:—

In 100 Parts.

Albumenoids	7.05
Starch	24.78
Sugar	12.35
Carbonaceous matter (non-nitrogenous) ..	47.05
Woody fibre	7.26
Potash (K ₂ O)	1.610
Soda (Na ₂ O)	0.340
Lime (CaO)	0.047
Magnesia (MgO)	0.158
Phosphoric acid (P ₂ O ₅)	0.224
Sulphuric acid (SO ₃)	0.052
Carbonic acid (CO ₂)	0.340
Chlorine (Cl)	0.032
Oxide of iron (Fe ₂ O ₃)	0.014
Silica (SiO ₂)	0.057
Oxide of manganese (MnO ₂)	0.004

= Ash, 2.92

From the small quantity of albumenoids or flesh-forming substances present in the banana, it cannot be considered by itself a convenient food, or even sufficiently nutritious for all the requirements of man. Under normal conditions the average man requires daily 4.2 ounces of albumenoids. To obtain this quantity from the banana fifteen pounds weight of the fruit would have to be consumed—a quantity altogether excessive and decidedly inconvenient, containing no less than nine pints, or over a gallon, of water.

In nutritive properties the Cavendish banana bears a

resemblance to the potato, as will be seen from the comparison following. It may be described as a very unevenly balanced food, not suited alone for the diet of man, but an excellent and wholesome addition to a diet rich in nitrogenous substances.

Comparison Analysis.

	Cavendish banana.	Potato.
Water	75.71	75.77
Albumenoids	1.71	1.79
Total carbonaceous matter (non-nitrogenous) ..	20.13	20.72
Woody fibre	1.74	0.75
Ash	0.71	0.97

VOLATILE FATTY ACIDS OF BUTTER.

By WILLIAM JOHNSTONE.

CONTINUING my research upon the composition of butter-fat, the following experiments are worth recording. A genuine butter yielding 85.6 per cent of insoluble fatty acids was operated upon, 5.433 grms. being taken and saponified in the usual manner for a Reichert-Wollny estimation of the volatile fatty acids.

During the distillation a quantity of solid volatile fatty acid collected in the condenser tube amounting to 0.273 grm., the iodine absorption of which was ascertained and gave the following results:—

Iodine solution taken	30.0 c.c.
Na ₂ S ₂ O ₃ equivalent to iodine taken	31.6 "
Na ₂ S ₂ O ₃ equal to oxidised remaining iodine ..	27.8 "

Na₂S₂O₃ equivalent to iodine absorbed .. 3.8

1 c.c. of Na₂S₂O₃ = 0.01203 grm. iodine.

$$\frac{3.8 \times 0.01203 \times 100}{0.273} = 16.74 \text{ per cent iodine absorbed.}$$

The distillation was continued upon the addition of more water until the flask broke, a further quantity of solid volatile acid having been obtained amounting to 0.332 grm., giving a total of 0.506 grm., equal to 9.31 per cent of solid volatile insoluble fatty acid. When the retort broke the fatty acids were distilling as rapidly as at the commencement of the experiment.

The 0.332 grm. was converted into a barium salt and extracted with ether, of which 0.355 grm. were taken, and dried at 100° C. for two hours, losing a m.grm. at 130° C. which, when ignited with sulphuric acid, gave 0.136 grm. BaSO₄:—

$$\frac{0.136 \times 100}{0.355} = 38.31 \text{ per cent BaSO}_4.$$

A further portion of this solid volatile fatty acid was converted into a lead salt, washed with alcohol, and then thoroughly extracted with ether; the lead salt insoluble in ether was decomposed, and the melting-point of the fatty acid taken, 53.2° C.; it was now dissolved in alcohol and made into an ammonia soap, and then precipitated with nitrate of silver, 0.456 grm. of the silver salt giving 0.1465 grm. of Ag equal to 32.12 per cent, myristic acid requiring by theory 32.23 per cent of silver; consequently the barium salt probably consisted of—

(C ₁₈ H ₃₃ O ₂) ₂ Ba ..	17.78	= 5.92 per cent BaSO ₄
(C ₁₄ H ₂₇ O ₂) ₂ Ba ..	82.22	= 32.41 " "

100.00 38.33

BaSO₄ found .. 38.31 per cent.

Or the solid fatty acids which collect in the condenser consists of—

18.6 per cent of pseudo-oleic acid.
81.4 " " myristic acid.

The volatile soluble fatty acids of this butter were converted into a barium salt and yielded in duplicate 73.57 and 73.61 per cent of barium sulphate, 1.8336 and 2.0464 grms. of the barium salt having been taken respectively for the estimation.

Butyric acid requires by theory 74.92 per cent BaSO_4 . The remainder of the soluble volatile fatty acid was then heated with bichromate of potash and sulphuric acid attached to upright condenser for two hours, the volatile acid then distilled off and converted into barium salt, 1.946 grm. of which gave 74.38 per cent BaSO_4 .

SIXTH REPORT OF THE COMMITTEE* APPOINTED FOR THE PURPOSE OF INVESTIGATING ISOMERIC NAPHTHALENE DERIVATIVES.

It was stated in the last report that Mr. Rossiter and the writer had devoted much time to the study of the dibromonaphthalenes, but that the results were not sufficiently complete to render their publication desirable; an account of the work contemplated in this passage was communicated to the Chemical Society late in the year (*cf. C. S. Proceedings*, 1891, p. 182).

In this communication, data were given which suffice to characterise and differentiate five of the isomeric dibromonaphthalenes, *i.e.*, the 1:4, 1:4', 1:3, 1:2' and 1:3' modifications. The action of bromine on α - and β -dibromonaphthalene was also described, and the nature of the complex product formed on *di*-brominating naphthalene, which has occupied the attention of so many observers, was finally determined, it being shown to consist of 1:4 dibromonaphthalene (m. p. 82–83°) mixed with the 1:4' isomeride (m. p. 132°).

When naphthalene is dibrominated, 1:4 dibromonaphthalene is the major product, so much so that this modification crystallises out in an almost pure state from the solution of the crude product in alcohol. It has been stated by Darmstaedter and Wichelhaus that when naphthalene- α -sulphonic acid is brominated, a product is obtained which on crystallisation from alcohol first affords 1:4' dibromonaphthalene, the remainder of the product melting at 68–70°, and resembling that obtained from naphthalene. It therefore seemed probable that whereas naphthalene yields chiefly 1:4 dibromonaphthalene, the α -sulphonic acid yields chiefly the 1:4' derivative, and that consequently the *acid*-radicle exercises a marked influence in determining the entrance of bromine into the unsubstituted nucleus (*cf. Report for 1886*), an influence much greater than that of bromine towards sulphuric acid, as bromonaphthalene yields little but the 1:4 acid when sulphonated. Darmstaedter and Wichelhaus's experiments have been repeated by the writer, and the accuracy of this conclusion confirmed; a very considerable amount of 1:4' bromosulphonic acid is formed on brominating naphthalene-sulphonic acid, 1:4 dibromonaphthalene being quite a minor product.

On comparing the dibromo-products obtained from naphthalene with the dichloro-products, an unusual divergence is apparent; there can be no doubt, however, that this is attributable to the extreme instability of bromine addition compounds of naphthalene. The dichloronaphthalenes are, in fact, products of the withdrawal of 2HCl from the tetrachloride, while the dibromonaphthalenes are products of the action of bromine on bromonaphthalene, and hence it is that the 1:3 modification, which is the chief product of chlorination, is absent from the product of bromination. When the conditions are similar the difference in behaviour of naphthalene towards chlorine and bromine is of the ordinary character,

and such as was to be expected; thus when α -chloronaphthalene is chlorinated by means of SO_2Cl_2 at such a temperature (100–180°) as to prevent the persistence of an addition compound, it yields pure 1:4' dichloronaphthalene and no trace of the 1:3 isomeride, which is the principal product of the hydrolysis of naphthalene tetrachloride. β -Chloronaphthalene in like manner yields a mixture of the 1:2 and 1:2' derivatives. The results of a series of experiments on the formation of chlorinated naphthalenes at high temperatures by means of SO_2Cl_2 and similar chlorinating agents which the writer and Dr. Wynne are engaged in carrying out will be given on a subsequent occasion; they desire, however, here to recognise the assistance which they have received from Mr. Jenks.

Finally, it may be mentioned that Mr. Rossiter and the writer, having repeated Meldola's experiments on the bromonitronaphthylamines, have been led to interpret this author's results in a manner somewhat different from that originally adopted by him, but in accordance with the results of more modern enquiries (*cf. C. S. Proceedings*, 1891, p. 186; Meldola, *C. S. Trans.*, 1892, p. 766).

A comprehensive survey of the very numerous recorded facts shows that "the laws of substitution" in the naphthalene series are in the main easy to decipher, and pervaded by a few very simple principles. The writer and Dr. Wynne hope during the coming year to discuss these in a comprehensive memoir, dealing with the investigation which they have conjointly carried on now during over six years. It is perhaps not undesirable to state that no single fact has yet been recorded serving to support the view advocated by Claus, that the structure of naphthalene is unsymmetrical. Whatever its exact inner structure may be, the two nuclei of naphthalene must be represented alike.

THE CONDITIONS OF THE FORMATION AND DECOMPOSITION OF NITROUS ACID.*

By V. H. VELEY, M.A.

(Continued from p. 177).

THESE results, in the case of acid of the concentration used, would seem to indicate that the phenomenon is not entirely one of solution, but partly also of reversible chemical changes, the difference in their relative intensities being greatest at or about 32°, and at least 52°, a temperature at which nitrous acid by itself would be very rapidly decomposed. These results were also confirmed by experiments conducted with a sample of acid of half the concentration of that used above.

Concentration of nitric acid = 0.1279 grm.

SERIES VII.—Temperature, 22.5°.

Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage ratio.
3	0.1257	0.0124	89.79 : 10.21
4	0.1276	0.0136	90.37 : 9.63

SERIES VIII.—Temperature, 32°.

3½	0.1203	0.0137	89.78 : 10.22
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SERIES IX.—Temperature, 42°.

3	0.1185	0.0114	91.22 : 8.78
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SERIES X.—Temperature, 52°.

3	0.1274	0.0088	93.54 : 6.46
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In these sets of experiments, also, the amount of nitrous acid formed increases up to a temperature of 32°, and from this point again decreases. Further, from compari-

* Consisting of Professor W. A. Tilden and Professor H. E. Armstrong (Secretary). (Drawn up by Professor Armstrong). Read before the British Association, Edinburgh Meeting, 1892, Section B.

* A Paper read before the Royal Society, June 2, 1892.

son of results obtained with the two samples of acid at the same temperature it is evident the percentage ratio of nitrous acid is *increased with decrease of concentration*. To confirm this a further series of experiments were conducted with an acid of one-fourth of the concentration of that used in the first set.

Concentration of acid = 0.0655 grm. in 1 c.c.

SERIES XI.—Temperature, 22.5°.

Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage ratio.
4½	0.0662	0.0097	87.22 : 12.78
2	0.0661	0.0088	88.25 : 11.75

SERIES XII.—Temperature, 32°.

3	0.0624	0.0097	86.55 : 13.45
2	0.0634	0.0105	85.79 : 14.21

SERIES XIII.—Temperature, 42°.

3	0.0630	0.0081	88.61 : 11.39
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SERIES XIV.—Temperature, 52°.

3	0.0652	0.0062	91.31 : 8.69
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The results given in the four tables above are perfectly in accordance with those of the preceding series, the maximum value for the amount of nitrous acid being as before, at a temperature of 32°; they also show that with decrease of concentration the percentage ratio of nitrous acid is increased, though its total amount is decreased. Experiments were then conducted with acids of greater concentration, the results of which are given below.

Concentration of acid = 0.3457 grm. in 1 c.c.

SERIES XVI.—Temperature, 22°.

Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage ratio.
3	0.3254	0.0268	92.39 : 7.61

SERIES XVII.—Temperature, 32°.

3	0.3253	0.0212	93.88 : 6.12
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SERIES XVIII.—Temperature, 42°.

3	0.3080	0.0173	94.68 : 5.32
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Concentration of acid = 0.6338 grm. in 1 c.c.

SERIES XIX.—Temperature, 22.5°.

3	0.5940	0.0397	93.74 : 6.26
3 (expt. repeated.)	0.5791	0.0408	93.42 : 6.58

SERIES XX.—Temperature, 32°.

3½	0.5306	0.0295	94.74 : 5.26
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The liquids obtained in the experiments detailed above were of a *blue* tint, but it was also observed that in the case of the more concentrated acids red fumes were evolved to a slight extent, thus showing under these conditions a more complex reaction than the simple reversible change given above. It is also to be noticed that the sum of the quantities of nitrous and nitric acids found are less than the quantity of nitric acid originally taken, thus showing that some unaccounted-for destruction of the acid had taken place. In a set of experiments with more concentrated acids the evolution of fumes and the destruction of the acid were further noticeable.

Concentration of acid = 1.089 grm. in 1 c.c.

SERIES XXI.—Temperature, 22.3°.

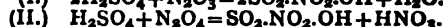
Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage ratio.
1½	0.8704	0.0632	93.25 : 6.75
2 (expt. repeated.)	0.8700	0.0664	92.91 : 7.09

SERIES XXII.—Temperature, 27°.

1½	0.7009	0.0391	94.72 : 5.29
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In the above series of experiments, when the nitric oxide gas was first passed in, a yellow colour was produced, but this speedily changed into a deep *green* tint. It thus appeared that nitrogen peroxide was at first produced and this was converted possibly by the nitric oxide and possibly, also, by the water present, into the green acid which certain writers have considered to have the composition $\text{N}_2\text{O}_3 \cdot \text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$; such an acid, however, would contain nearly 50 per cent of nitrous acid.

After most of the experimental work above detailed had been performed, a paper appeared by F. Marchlewski (*Ber. Deut. Chem. Gesell.*, vol. xxiv., p. 3271), entitled "Zum Kenntniss der verschiedenen Färbungen der Saltpetersäure," in which the author describes various experiments upon the reaction between nitric oxide and nitric acid. The main object of the paper was to determine the composition of the various coloured liquids produced when nitric oxide, nitrous fumes, and nitrogen peroxide are passed into nitric acid of different concentration. The method employed consisted in preparing such liquids and then decolourising them by a current of carbonic anhydride; the gases evolved were passed into sulphuric acid and the solution subjected to analysis. The process is based upon the observations of Lunge that nitrous fumes give under these conditions nitrosyl sulphuric acid, while nitrogen peroxide gives a mixture of nitrosyl sulphuric and nitric acids, thus:—



It might appear open to question whether the composition of these liquids can be ascertained by this indirect method, and whether a liquid apparently decolourised contains nothing but the residual nitric acid (more or less diluted) of the operation. My own experience has shown that it is extremely difficult to remove the last traces of the yellow colour from the more concentrated acids; though, on the other hand, it must be allowed that the method of analysis adopted in the text would not distinguish between nitrous acid, on the one hand, and nitrogen peroxide on the other, the latter of which would appear in the course of analysis as an equimolecular mixture of nitrous and nitric acids. These remarks would, however, apply probably only to the two last series of experiments. Marchlewski gives no observations of time, temperature, or degree of humidity of gases, whether oxides of nitrogen or carbonic anhydride, nor a single control analysis of the residual nitric acid. Some proof is given that the difference between the *green* and *blue* acids is dependent upon not only the water present, but also upon the dissolved nitric oxide. Marchlewski seems to be quite unaware of the observations of Péligot*, made nearly forty years ago, upon the same subject.

Certain experiments were made upon the action of dry nitric oxide upon nearly anhydrous nitric acid (specific gravity $7/7^\circ = 1.5326$), the preparation of which has been described in a previous section. The air was driven out of the apparatus by a current of carbonic acid dried by passage through a wash-bottle containing concentrated sulphuric acid, and then through three drying tubes filled with pumice and phosphorus pentoxide. The nitric acid was contained in the Geissler's bulbs as before (kept at a temperature of 11°), and subsequent to them was another wash-bottle of sulphuric acid to prevent the access of moisture by backward diffusion.

On passage of the nitric oxide gas, the portion of acid in the first bulb was turned a yellow tint, which gradually deepened to an orange-red; when about a litre of

* *Ann. Chim. Phys.*, [III.], vol. ii., p. 58. The remarks of Péligot seem worth transcribing, as having possibly fallen into undeserved oblivion: "Comme l'acide azotique pur paraît être bleu tandis que l'acide azotique et l'acide hypoazotique mélangés sont jaunes on obtient par cette action de l'eau" (viz., upon nitrogen peroxide) "selon les proportions employées les différents nuances de vert et de bleu . . . qui se développent également par l'action de bioxyde d'azote sur l'acide azotique à différents degrés de densité. Le produit vert . . . se forme aussi par le contact du bioxyde d'azote avec l'acide hypoazotique, et sa production pouvait être tout à fait indépendante de l'eau" (as shown by experiment).

the gas had been driven through a red oil appeared floating upon the surface of the acid, and a few minutes after the red oil turned a green tint, and for some time there were two distinct liquids of different densities in the bulb, but afterwards a green uniform liquid was obtained. Meanwhile the portion of acid in the second bulb had deepened in tint, then the red oil was formed, and the other phenomena in due succession. (The weight of the acid at this point had increased). When about 4 litres of nitric oxide had passed in the green liquid in the first bulb gradually turned to a blue, which slowly evaporated into the second bulb, and eventually only a few drops of an almost colourless liquid were left. Simultaneously the portion of acid in the third bulb showed the transition tints of yellow to orange with ultimate formation of the red oil, and also dense red fumes passed out of the acid. At this point the experiment was stopped, and the weight of the nitric acid was found to have considerably decreased.

The explanation of these changes, which were observed in part by Priestley* at the end of the last century, seems to be as follows:—At first nitrogen peroxide is formed by the mutual oxidation of the nitric oxide and reduction of the nitric acid, and this is retained in solution by the excess of the acid, $2\text{HNO}_3 + 2\text{NO} = 3\text{N}_2\text{O}_4 + 2\text{H}_2\text{O}$. A point is reached at which the acid becomes super-saturated, and the excess of the peroxide separates out (the red oil). According to the experiments of Péligot, nitric oxide passed into this gives a green liquid. The absorption and retention of the nitrogen peroxide accounts for the gain in weight (about one-sixth) of the acid. The reduction then proceeds further, and nitrous acid (the blue liquid) is produced, thus: $\text{N}_2\text{O}_4 + 2\text{NO} + 2\text{H}_2\text{O} = 4\text{HNO}_2$, and this is evaporated by the continued current of the nitric oxide, leaving finally only the water originally present, both free and combined, in the nitric acid. This destruction of the nitric acid accounts for the loss in weight. As Priestley wrote: "Towards the end of the process (of absorption of nitrous air by pale-yellow spirit of nitre), the evaporation of the acid was perceived to be very great, and when I took it out the quantity was found to be diminished by one-half. Also, it had become by means of the process and evaporation together, exceedingly weak, and was rather blue than green."

Reaction between Nitric Oxide and Mercuric Nitrate in Nitric Acid Solution.

In my former paper (*Phil. Trans.*, 1891, A, p. 315), it was shown that when a current of hydrogen was passed through a solution of mercuric nitrate in nitric acid solution the mercuric was reduced to a mercurous salt without any considerable formation of nitrous acid, which was, however, produced in abundance when cupric nitrate was subjected to the same action. As it seemed probable that the nitrous acid which might have been produced in the former operation was in reality used up in the reduction of the mercuric salt, the experiment was repeated in precisely similar manner, nitric oxide being substituted for hydrogen. It was found, as before, that the mercuric salt was reduced; from 0.5 grm. mercuric oxide dissolved in nitric acid (1 c.c. containing 0.2549 grm. acid) after passage of nitric oxide for $3\frac{1}{2}$ hours at a temperature of 35° , 0.019 grm. of mercurous chloride was obtained, while from a similar portion, through which the nitric oxide had not been passed, 0.0018 grm. was precipitated. It is probable, then, that the hydrogen in the former experiments reduced at first the free nitric into nitrous acid, which in its turn reduced the mercuric nitrate, thus: $2\text{Hg}(\text{NO}_3)_2 + 2\text{HNO}_2 = \text{Hg}_2(\text{NO}_3)_2 + 2\text{HNO}_3$. No free nitrous acid would therefore appear in the course of the operation.

(To be continued).

ON THE REACTIONS OF FERRIC SALTS WITH SULPHOCYANATES.

By H. M. VERNON, B.A.

(Continued from p. 179).

The Reactions of other Ferric Salts and Sulphocyanates.

In addition to the reactions of ferric chloride with potassium sulphocyanate, those of other ferric salts with other sulphocyanates were also studied. The object was to determine what change of colour effect was produced by varying the ferric salt on the one hand and the sulphocyanate on the other, and thus to obtain an insight as to the reactions taking place in the solutions. The ferric salts examined besides the chloride were the nitrate, sulphate, tartrate, acetate, and citrate. A solution of ferric nitrate was prepared by evaporating down to dryness on the water-bath a solution of ferric oxide in nitric acid. The percentage of ferric oxide in the salt was determined by ignition. It was found to contain 5.55 per cent more Fe_2O_3 than is required by the formula $\text{Fe}_2(\text{NO}_3)_6$, so the amount of standard nitric acid required to bring it to the correct percentage was added to its solution. Solutions of the tartrate, citrate, and acetate of iron were prepared by decomposing ferric sulphate with the theoretical quantities of the corresponding barium salts. By this means solutions were obtained containing scarcely any of the free acids, whilst if the solutions are evaporated to dryness and the salts so obtained dissolved up again, ferric oxide is deposited, and solutions containing considerable quantities of free acids are obtained. Besides the reactions of potassium sulphocyanate, those of the sulphocyanates of ammonium, sodium, lithium, calcium, and barium were examined. The potassium and ammonium salts used were obtained from the manufacturer in as pure a state as possible, but they were not further purified. The sodium, calcium, and barium salts were prepared by boiling aqueous solutions of the hydrates of these metals with the theoretical quantities of ammonium sulphocyanate, whereby all the ammonia was driven off. The solutions were then evaporated down and crystallised. The lithium salt was prepared by decomposing lithium sulphate with barium sulphocyanate. The calcium and lithium salts did not crystallise well, but after evaporating down the solutions to dryness on the water-bath, both set on cooling to white semi-solid masses.

The colour effects produced by mixing solutions of the various ferric salts named with those of the sulphocyanates were then determined. Two series of determinations were made: one with solutions containing a hundred equivalents of ferric salt to one equivalent of sulphocyanate; these were examined at dilutions of 160, 320, and 800 litres; the other, with solutions containing one equivalent of ferric salt to one equivalent of sulphocyanate, being examined at dilutions of 40, 80, and 160 litres. No determinations of solutions containing 100 equivalents of sulphocyanate were made for several reasons. In the first place, the previous experiments with ferric chloride and potassium sulphocyanate showed that the reactions taking place in solutions containing excess of sulphocyanate are somewhat complex, and do not take place in accordance with the law of mass, and also that these solutions are not nearly so stable as regards dilution as those containing excess of ferric salt. It is probable therefore that the colour values obtained with these solutions are due to the effects of several causes, and these may vary to different extents with different sulphocyanates, so that the values obtained would not express the true amount of reaction taking place between the salts; also it was found that sulphocyanate solutions showed slight variations in colour effect on standing, and showed slightly different colour values, according as the ferric salt was added to the sulphocyanate or *vice versa*. On standing some minutes, however, these solutions showed the same colour

* "Experiments and Observations on Different Kinds of Air," vol. i., p. 383. I may be allowed to allude to the section of this work relating to nitrous acid, which contains a number of observations upon its properties; several of them appear to have been published as novelties many years afterwards.

Salt.	Dilution in litres.	For solutions containing to 100 parts of ferric salt 1 part of sulphocyanate of—						Mean colour- constants for ferric salts.
		Potassium.	Ammonium.	Sodium.	Lithium.	Calcium.	Barium.	
Ferric chloride ..	160	9'5 X 17'2	10'0 X 15'9	10'0 X 14'6	10'0 X 10'0	11'0 X 12'2	10'0 X 12'7	10'08
" "	320	9'5 X 16'7	10'0 X 15'4	10'0 X 13'8	10'0 X 9'4	11'0 X 11'1	10'0 X 11'8	10'08
" "	800	10'0 X 14'4	10'0 X 13'0	10'0 X 12'0	10'0 X 7'5	11'0 X 10'6	10'0 X 10'2	10'17
" nitrate ..	160	10'5	9'7	10'0	10'5	10'4	10'4	10'25
" "	320	10'5	9'8	10'2	10'7	11'4	10'6	10'53
" "	800	11'3	10'0	10'2	10'9	10'6	10'6	10'60
" sulphate..	160	6'97	6'55	6'90	6'31	6'68	—	6'67
" "	320	6'36	6'20	6'77	6'22	6'82	—	6'47
" "	800	6'17	5'52	6'25	5'74	5'19	—	5'73
" tartrate ..	160	4'89	4'20	4'25	3'67	3'93	—	4'18
" "	320	3'99	3'45	3'80	3'16	3'18	—	3'52
" "	800	2'89	2'36	2'55	2'65	2'26	—	2'54
" acetate ..	160	2'05	1'82	2'01	2'00	1'64	—	1'90
" "	320	2'02	1'24	1'90	1'94	1'50	—	1'72
" "	800	1'98	1'25	1'08	1'74	1'05	—	1'42

For solutions containing to 1 part of ferric salt 1 part of sulphocyanate.								
" chloride ..	40	9'0 X 7'02	11'0 X 5'72	11'0 X 5'25	10'0 X 2'92	10'6 X 4'88	9'0 X 4'51	9'93
" "	80	9'0 X 4'08	10'0 X 3'52	10'0 X 2'78	10'0 X 1'31	10'6 X 2'43	9'0 X 1'90	9'77
" "	160	10'0 X 1'86	10'0 X 1'23	10'0 X 1'01	10'0 X 0'81	10'6 X 0'98	9'0 X 0'82	9'77
" nitrate ..	40	10'4	11'8	11'7	11'3	11'3	11'4	11'31
" "	80	11'0	11'4	12'8	11'6	11'4	11'6	11'63
" "	160	10'2	11'3	12'8	10'0	10'7	11'5	11'05
" sulphate..	40	7'51	7'97	6'44	6'13	6'64	—	6'94
" "	80	7'01	5'77	5'46	6'86	6'60	—	6'34
" "	160	6'24	7'32	8'02	7'78	6'95	—	7'26
" tartrate ..	40	2'78	2'52	2'63	2'60	2'34	—	2'57
" "	80	2'35	2'21	2'84	3'0	2'72	—	2'62
" citrate ..	40	2'35	2'08	2'17	2'23	1'84	—	2'13
" "	80	2'08	2'02	2'41	2'90	2'26	—	2'33
" acetate ..	40	1'74	1'59	1'75	2'55	1'74	—	1'87
" "	80	2'01	2'00	2'34	3'05	2'68	—	2'42

effect. With solutions containing excess of ferric salt, this was not the case. Solutions containing seven or more equivalents of ammonium sulphocyanate, when originally made up, gave colour values not far below those of the corresponding potassium sulphocyanate solutions, but on standing about half an hour or more they became quite colourless. It is probable that the ferric sulphocyanate dissolves in the excess of ammonium sulphocyanate, forming a kind of double salt; whatever it may be due to, it serves to emphasize the untrustworthiness of results obtained for solutions containing excess of sulphocyanate.

In the table are given the results obtained. The numbers are in this case compared with a different standard from those obtained in the former series, the colour effect of a solution containing to one equivalent of lithium sulphocyanate 100 equivalents of ferric chloride at a dilution of 160 litres being taken as 100, and the other values compared with this. In order to examine whether the colour values are the products of two numbers—one depending on the nature of the ferric salt, and the other on the nature of the sulphocyanate—arbitrary numbers are taken as the values due to each of the sulphocyanates at each dilution, and these are divided into the colour values obtained with the different ferric salts. It will be seen that the colour constants due to ferric chloride with the different sulphocyanates are taken as about the value 10 at all dilutions, whilst the colour constants due to the sulphocyanates are considered to vary with the dilution. Thus with ferric chloride and sodium sulphocyanate, for instance, in the 100 equivalent solutions, the numbers 14'6, 13'8, and 12'0 are taken as the colour constants due to the sodium sulphocyanate at dilutions of 160, 320, and 800 litres respectively, and these numbers are divided into the colour values obtained with sodium sulphocyanate and the other ferric salts. Each ferric salt should have the same constant colour equivalent, irrespective of the sulphocyanate it is reacting with. From the table it will be seen that such is the case, allowing for experimental error, which in colorimetric work must necessarily be

large. With ferric chloride the extreme values vary from 9'5 to 11'0; with ferric nitrate, from 9'7 to 11'4; with ferric sulphate, from 5'19 to 6'97; with ferric tartrate, from 4'89 to 2'26; with ferric acetate, from 2'05 to 1'05. It must be remembered that these variations are in great part due merely to the fact that all ferric sulphocyanate solutions are not equally affected by dilution. Thus it is evident from the last column of the table, which gives the means of the colour constants of the different ferric salts at each dilution, that whilst ferric chloride and ferric nitrate solutions are affected about equally by dilution, those of ferric acetate are affected more, whilst those of ferric sulphate and ferric tartrate are affected to a still greater extent. The different behaviour is easily accounted for when it is remembered that hydrochloric and nitric acids are monobasic acids, whilst sulphuric and tartaric acids are dibasic. With ferric sulphate and tartrate solutions a decrease of colour would occur owing to the greater formation of the acid salts in the more dilute solutions. Ostwald has shown by electro-chemical methods ("Lehrbuch," ii., 831) that the relative affinities of monobasic to dibasic acids vary according to the dilution. It will be shown later that the great decrease of the colour constants of ferric tartrate on dilution are only partly due to this cause. If the colour equivalents at a dilution of 160 litres only be taken, the extreme values for ferric nitrate vary from 10'5 to 9'7; for ferric sulphate, from 6'97 to 6'31; for ferric tartrate, from 4'89 to 3'67; for ferric acetate, from 2'05 to 1'64.

In these reactions the colour of the ferric salt was in all cases but that of the acetate so slight compared with that of the ferric sulphocyanate formed that it was not allowed for. With ferric acetate the colour is so deep and the amount of ferric sulphocyanate formed in solution so small that if one hundred equivalents are taken, almost two-thirds of the colour effect of the solution is due to this cause alone. The accuracy of the determination of the ferric sulphocyanate formed would thus be considerably impaired, so only 50 equivalents of the acetate were taken. About half the colour effect of the solution was

then due to this cause. This was of course determined and allowed for. The experiments with ferric chloride and potassium sulphocyanate show that in concentrated solutions the colour values of solutions containing only thirty equivalents of ferric salt are only very slightly smaller than for one hundred equivalent solutions, so the colour constants for ferric acetate solutions at dilutions of 160 litres and 320 litres can only be very slightly decreased from this cause. At a dilution of 800 litres they must be appreciably smaller.

(To be continued.)

ACTION OF SULPHUR IN PRESENCE OF WATER UPON THE SALTS FORMED BY THE POLYBASIC ACIDS.*

By J. B. SENDERENS.

(Concluded from p. 183).

(a) *Arsenates*.—The action of sulphur in presence of water upon the ortho-arsenates presents great analogies to that which it exerts upon the phosphates. Still, there is this distinction, that whilst phosphoric acid remains unaltered during all the reactions, arsenic acid is sometimes decomposed. Thus with the trisodium and disodium arsenates we obtain sulpharsenates and oxy-sulpharsenates, the formation of which is easily explained. In fact, sulphur yields at first with these two arsenates, as with the corresponding phosphates, a thio-sulphate and a polysulphide which, on decomposition, yields hydrogen sulphide. This latter gas acts upon the undecomposed arsenates so as to produce sulpharsenates and oxy-sulpharsenates.

If we take this peculiarity into account, the analogy between the arsenates and the sulphates may be traced throughout. Thus the action of the sulphur ceases at the sesquibasic compound for the alkaline arsenates, but for those of the alkaline earths continues to the bibasic salt. Silver and copper arsenates are totally decomposed by sulphur, whilst the lead and nickel arsenates absolutely resist its action.

(b) *Alkaline Arsenates*.—Sulphur decomposes with boiling solutions of neutral and acid sodium arsenite. It acts at first upon the soda, forming a polysulphide, which is then decomposed with a liberation of hydrogen sulphide. This latter substance forms, with arsenious acid, arsenic trisulphide, which remains in the hot liquid, and is deposited on cooling. Sodium sulpharsenate is formed at the same time. These reactions are limited by an inverse action, that of the transformation of arsenic sulphide in contact with boiling water into arsenious acid and hydrogen sulphide, which explains the development of sulphuretted hydrogen all the time of the experiment.

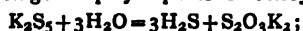
(c) *Alkaline Chromates*.—The action of sulphur upon solutions of these salts was explained in a former communication.

With neutral potassium chromate there is produced an alkaline polysulphide which is decomposed with the formation of sulphuretted hydrogen. The reaction is determined by the free potassa of the dissolved chromate, which yields with sulphur a polysulphide and thio-sulphate.

The chromic acid, on its part, is attacked by the sulphur, with the formation of chromium hydroxide. This first experimental stage is shown by the equation—

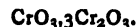


In a second stage the polysulphide is destroyed.



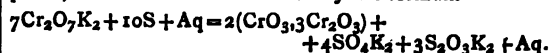
when the development of sulphuretted hydrogen commences.

With potassium bichromate we do not detect the slightest liberation of H_2S , and at no moment of the experiment does the solution contain a sulphide. This consequently excludes the action of sulphur upon the potassa of the bichromate, and establishes the strong acid function of chromic acid in potassium bichromate. According to Sabatier, chromic acid must have two functions: one of a strong acid, which appears in the formation of the bichromate; the other of a weak acid, as regards the mol. of alkali which transforms the bichromate into neutral chromate. The solutions of the neutral salt, according to Sabatier, contain neutral chromate, bichromate, and free alkali. These conclusions are confirmed by the action of sulphur upon the solutions of neutral chromate and of potassium bichromate. With the latter salt, there is formed a maroon-coloured precipitate of the composition—



This is a chromium chromate which has not yet been described.

The liquid contains potassium sulphate, and thio-sulphate, and the reaction is shown by the formula—



(d) *Alkaline Manganates*.—The action of sulphur upon the solution of these salts presents the same peculiarities as with the chromates.

Potassium permanganate is decomposed according to the equation—



Potassium permanganate is reduced by sulphur at the ordinary temperature, yielding a hydrated manganese peroxide and potassium sulphate.

NEW METHODS FOR QUANTITATIVE ANALYSIS.*

By A. BAUMANN.

(Continued from p. 182).

Determination of Chromic Oxide.

THE above method of determining chromic acid may also be used for an accurate determination of chromic oxide, since it is not difficult to convert chromic oxide into chromic acid. For the oxidation of the salts of chromic oxide it is preferable to use hydrogen peroxide in an alkaline solution. After the oxidation is completed, the excess of hydrogen peroxide is completely destroyed by boiling the alkaline liquid, and after neutralisation with sulphuric acid the chromic acid is destroyed by gas-volumetry.

In the analysis of chrome-iron ore, the mineral must not be opened up by fusion with soda and nitre, since large quantities of nitric acid interfere with the accurate determination of chromic acid.

We may, instead, use with advantage the process of L. P. Kinnicutt and G. W. Patterson, in which the mineral is ignited with sodium carbonate and barium peroxide, and then decomposed, not with hydrochloric acid, but with sulphuric acid.

3. *Determination of Sulphuric Acid*.—According to L. W. Andrews and H. Quantin, sulphuric acid may be effected by determining a quantity of chromic acid equivalent to the sulphuric acid. This indirect determination can, according to Baumann, be very easily executed in a gas-volumetric manner. Here, also, a solution of barium chromate comes in use.

The liquid in question, which must not contain too large an excess of hydrochloric acid, and only very small quantities of nitric acid and nitrates, is placed in a

measuring flask holding 100 c.c. and precipitated in the cold with a solution of barium chromate in hydrochloric acid. The liquid is shaken up, allowed to stand for a short time (about thirty minutes), diluted with water to about 90 c.c., mixed with ammonia until the reaction is alkaline, filled up to the mark, and, after shaking, filtered through a dry double-folded filter. From 25 to 60 c.c. of the filtrate (according to the quantity of the chromic acid) are poured into the gas-generating vessel of the azotometer, 10 c.c. of sulphuric acid are added, and the chromic acid is determined with hydrogen peroxide in the manner already described. One c.c. oxygen at 0° and 760 m.m. barometric pressure corresponds to 1.787636 m.grms. SO_3 , or 1 m.grm. oxygen corresponds to 1.2509 m.grms. SO_3 .

In liquids containing salts of copper, so much ammonia must be added for neutralisation that the precipitate of copper formed at first is re-dissolved; instead of 10 c.c. sulphuric acid, 20 c.c. are then used for the determination.

The barium chromate to be employed must before use be repeatedly boiled up with water and then washed until the last washings no longer give a precipitate with barium chloride.

As the method yields excellent results, especially in the case of very small quantities of sulphuric acid, it may be particularly suitable for the determination of this acid in water, and principally in drinking-water; but in ash, and in substances which contain much phosphoric acid, the determination cannot be undertaken directly in the hydrochloric solution, since on neutralising with barium chromate, barium phosphate is simultaneously deposited.

The phosphoric acid must therefore be eliminated before the determination. In ashes this is effected by extraction with boiling water. The watery solution is then used at once, and the hydrochloric acid is simply neutralised. If the phosphoric acid is present in the form of an alkaline salt, it is precipitated by means of magnesia mixture. This precaution is necessary only if a considerable quantity of phosphoric acid is present. Very small quantities do not affect the accuracy of the analysis.

(To be continued).

THE SYNTHESIS OF SUGARS.*

By W. E. STONE, Purdue University.

(Concluded from p. 180).

It now remained to establish a connection between the synthetic sugars and the most common of the natural sugars, the grape sugar or dextrose. This is a stereoisomer of mannose (*Berichte D. Ch. G.*, xxiii., 2133); moreover their "osazons" are identical, which would show that their isomerism depends upon the asymmetry of the carbon atom indicated by the asterisk in the following formula (*Berichte D. Ch. G.*, xxii., 374) —



So slight a difference as this it would seem possible to overcome, although the sugars themselves are too easily decomposed to withstand such a reaction. But by heating the respective acids derived from these sugars (mannonic and gluconic) with chinolin or pyridin to 140°, it was found that the gluconic acid was converted, in part, into d. mannonic acid, and *vice versa*, the d. mannonic acid into gluconic acid. The latter was readily reduced to d. glucose, and thus the synthetic connection with the most important member of the hexatomic sugar group established. In the same way the l. mannonic acid, which it will be remembered is identical with the arabinose carbonic acid, was converted into l. gluconic acid, and this, by reduction, into l. glucose. Also, by

combining equal molecules of the d. and l. gluconic acids, there was obtained an inactive gluconic acid, which was reduced to i. glucose. The latter was also obtained by combining the d. and l. glucose, and was characterised as a syrup that fermented with yeast (*Berichte D. Ch. G.*, xxiii., 2620). It was interesting to note here that the yeast destroyed the d. glucose, or that which is ordinarily fermented in nature, rejecting the synthetic sugar precisely as in the case of the i. fructose.

This completed the series of optical isomers of the hexatomic sugar group, and showed them all to be derivatives of mannit. The list includes about twenty bodies, all produced synthetically from formaldehyd. Of these, four had been previously known as occurring in Nature, *vis.*, mannit, sorbit, glucose, and fructose. All fall into three optical classes, dextro- and lævo-rotatory and inactive. As regards their chemical constitution they include four isomeric alcohols ($\text{C}_6\text{H}_{14}\text{O}_6$),—sorbit, and d., l., and i. mannit; nine isomeric aldehyd or ketone sugars ($\text{C}_6\text{H}_{12}\text{O}_6$),—d., l., and i. fructose, d., l., and i. mannose, and d., l., and i. glucose; and six isomeric, monobasic oxy-acids ($\text{C}_6\text{H}_{12}\text{O}_7$),—d., l., and i. mannonic acids, and d., l., and i. gluconic acids. The accompanying diagram shows the synthetic relation of these to each other (see next page).

The synthesis of glucose is regarded by Fischer as the most important of all this work. He suggests that many of these synthetical products will be found in Nature. It is, however, significant that thus far only the sugars of the d. series have been found in Nature, while the first direct product of the synthesis was the inactive fructose. The course, even in a roundabout way, from formaldehyd to glucose, is regarded as important support for the theory of Von Baeyer for the formation of glucose in green plants. So also, in animal physiology, there are indicated the possibilities to be attained from the knowledge obtained concerning the structure and sources of the different sugars. For instance, the new bodies may possess nutritive values different from those of the sugars heretofore known and studied; their assimilation products may be different; and further, the sugars with more or less than six carbon atoms may produce in the animal or vegetable organism new kinds of fats and oils, or new forms of albumen. These ideas are of course speculative, but worthy of consideration.

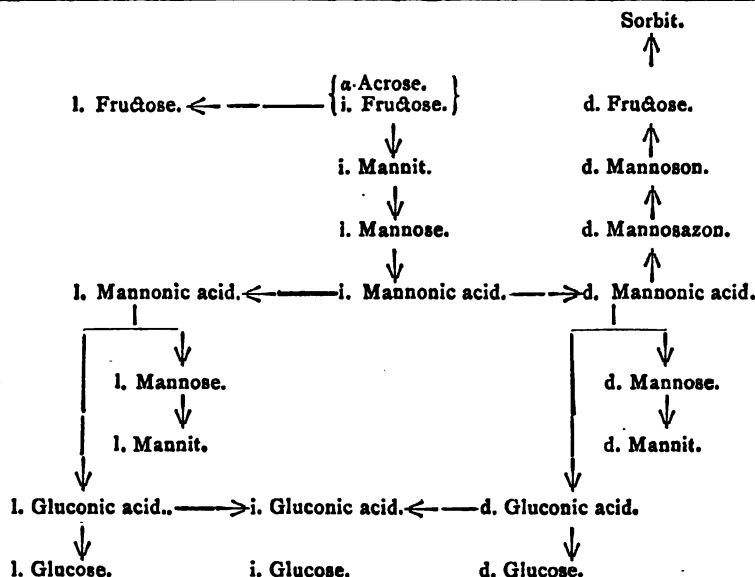
As is well known, the continued oxidation of glucose yields the dibasic saccharic acid, $\text{C}_6\text{H}_{10}\text{O}_8$, or—



Like the monobasic acids it forms a lacton which, on reduction by sodium amalgam as already described, yields an aldehyd acid, $\text{COOH}(\text{CHOH})_4\text{CHO}$, in which the carboxyl group, formerly typical of gluconic acid, has been reduced (*Berichte D. Ch. G.*, xxiii., 937). This product was found to be identical with glucuronic acid, and the synthesis of this interesting body thus established. By continued reduction the aldehyd group was reduced to an alcohol group, $\text{COOH}(\text{CHOH})_4\text{CH}_2\text{OH}$, and the new acid thus obtained was called *gulonic acid*. From this it was but a step, by means of the sodium-amalgam reduction, to a new sugar *d. gulose* which was not fermentable, or at least only with difficulty (*Berichte D. Ch. G.*, xxiv., 521). From this it appears that the *dibasic acids* derived from the sugars again offer a fruitful source for new synthetic sugars.

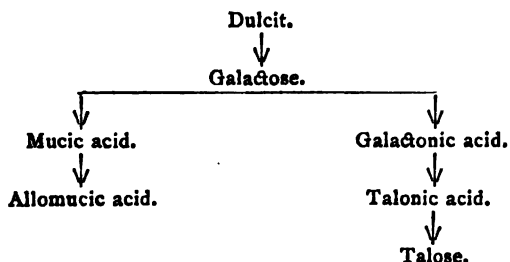
Making use of the addition of hydrocyanic acid to the aldehyds, as already described in connection with arabinose, Fischer has built up from the hexatomic sugars a series of new sugars with seven, eight, and nine carbon atoms. For instance, from d. glucose was obtained the d. glucose-carbonic acid, $\text{CH}_2\text{OH}(\text{CHOH})_5\text{COOH}$, which on reduction became gluco-heptose, $\text{C}_7\text{H}_{14}\text{O}_7$, and this in turn was built up to gluco-octose, $\text{C}_8\text{H}_{16}\text{O}_8$ (*Berichte D. Ch. G.*, xxiii., 934). Only lack of material prevented an indefinite extension of this synthesis. A similar series was obtained from d. mannose and galactose, and might

* *Agricultural Science*, vi., No. 4.



undoubtedly be had also from the l. and i. mannoses and glucoses. A noteworthy feature of the sugars thus far obtained is, that those containing three atoms of carbon or multiples of that number are fermentable, while the others are not. Glycerose, $C_3H_6O_3$, fructose, mannose, and glucose, $C_6H_{12}O_6$, and manno-nonose and glucononose, $C_9H_{18}O_9$, ferment easily.

The work thus far described had been confined to the mannit series. Of the corresponding isomeric hexatomic alcohol, dulcit, $C_6H_{14}O_6$, only one derived sugar had thus far been known, viz., galactose. This yields, on oxidation, the monobasic galactonic acid, $C_6H_{12}O_7$. After the successful conversion of mannonic into gluconic acid, Fischer made the same attempt with galactonic acid by heating to 140° – 150° with chinolin or pyridin, and obtained a similar result. The galactonic acid was transformed into an isomer, called talonic acid, which on reduction gave a corresponding sugar *talose* (*Berichte D. Ch. G.*, xxiv., 362). In the same way the dibasic mucic acid, $C_6H_{10}O_8$, derived from galactose by stronger oxidation, was transformed, by heating with pyridin, into allomucic acid, the farther derivatives of which have not yet been studied (*Berichte D. Ch. G.*, xxiv., 2136). The following diagram will illustrate the achievements thus far secured in the dulcit series:—



Fischer's researches have also included the group of pentatomic sugars, which had heretofore consisted only of arabinose and xylose ($C_5H_{10}O_5$). It will be remembered that the arabinose carbonic acid was recognised as the optical antipode of d. mannonic acid, i. e., l. mannonic acid. In the same way the xylose-carbonic acid was found to be the optical antipode of the d. gulonic acid derived from gluconic acid. This l. gulonic acid gave on reduction, in the

usual way, a sugar which was the optical isomer of d. gulose, and was called l. gulose (*Berichte D. Ch. G.*, xxiv., 528). Like the d. gulose it was non-fermentable. The l. gulose was further reduced to its corresponding hexatomic alcohol, $C_6H_{14}O_6$, and this was found on careful examination to be the l. sorbit (*Berichte D. Ch. G.*, xxiv., 2144), isomeric with the d. sorbit obtained from the d. fructose.

From their ability to combine with hydrocyanic acid, arabinose and xylose are shown to be regular oxaldehyds belonging respectively to the l. mannit and l. sorbit series. Their characteristics are supposed to depend upon differences in structure, which may be expressed in the following way by the different location of the aldehyd groups:—



But in accordance with this structure they should be converted by reduction into the same pentatomic alcohol, $C_5H_{12}O_5$. Curiously enough this is not the case, the products being quite different, and it is evident that the true relation of these sugars has not yet been discovered.

Like all the aldehyd sugars, arabinose and xylose are converted by mild oxidation into monobasic acids, $C_5H_{10}O_6$. These acids, by analogy with the d. mannonic and d. gluconic acids, may be expected to undergo a transformation into their stereoisomers on heating with pyridin. Thus far this hypothesis has only been proven in the case of the arabinic acid, which yielded an isomer called *ribonic acid*, which was reduced to a new pentatomic sugar *ribose*, $C_5H_{10}O_5$. This has been but little studied, but its "osazon" melted at 154 – 155° , and it yielded a marked quantity of furfural (*Berichte D. Ch. G.*, xxiv., 4214). Studies are now in progress with the dibasic acids of the pentose sugars, which will undoubtedly result in extending the number of this group.

The discovery of so many new sugars of such close relation to each other necessitates a more systematic nomenclature than has heretofore obtained. The system proposed by Fischer classifies the sugars into groups according to the number of carbon atoms which they contain, viz., triose, tetrose, pentose, hexose, heptose, octose, nonose, &c. (*Berichte D. Ch. G.*, xxiii., 2136). The proposition of Scheibler to call sugars of the formula $C_{12}H_{22}O_{11}$ "bioses," and of the formula $C_{18}H_{32}O_{16}$ "trioses" (*Berichte D. Ch. G.*, xviii., 646), is disposed of

by designating them respectively as hexobioses and hexotriosos, since they are easily decomposed to sugars of the hexose group. Again, the aldehyd or ketone sugars are specified by the terms "aldose" or "ketose." The old and well-established names dextrose and levulose lose their significance in this classification, these bodies being respectively designated by the names glucose and fructose.

The following list includes all of the known and well identified simple sugars, both natural and synthetic. Those which were known in nature or as direct derivatives of naturally occurring carbohydrates previous to Fischer's syntheses are printed in italics, by which the extent of his work is emphasised. In this list many little studied and not well characterised sugars, of occasional appearance in current literature, are not included.

- Triose group, $C_3H_6O_3$:—
Glycero~~se~~.
Tetrose group, $C_4H_8O_4$:—
Erythro~~se~~.
Pentose group, $C_5H_{10}O_5$:—
Arabino~~se~~,
Xylo~~se~~,
Rhamno~~se~~ (methyl-pentose, $CH_3C_5H_9O_5$),
Ribo~~se~~.
Hexose group, $C_6H_{12}O_6$:—
d., l., and i. gluco~~se~~,
d., l. gulose,
d., l., and i. manno~~se~~,
d., l., and i. fru~~ctose~~,
Sorbo~~se~~,
Galacto~~se~~,
Talo~~se~~,
Formo~~se~~,
Rhamno-hexose (methyl-hexose).
Heptose group, $C_7H_{14}O_7$:—
Manno-hepto~~se~~,
Gluco-hepto~~se~~,
Fru~~cto~~-hepto~~se~~,
Gala-hepto~~se~~,
Rhamno-hepto~~se~~ (methyl-hepto~~se~~).
Octose group, $C_8H_{16}O_8$:—
Manno~~octose~~,
Gluco~~octose~~.
Nonose group, $C_9H_{18}O_9$:—
Manno~~nonose~~.

Of the thirty sugars mentioned twenty are the result of Fischer's research, and to these may be added the dozen new alcohols, arabit, xylit, and l. sorbit, and some dozen or more of the various related acids which he has either discovered outright or has been the first to recognise in their true relations. It is not over-estimating the value of this work to characterise it as the greatest contribution yet made to the knowledge of the sugars.

Domestic Electric Lighting.—Messrs. H. Alabaster, Gatehouse, and Co. have now in the press, shortly to be issued, a new work entitled "Domestic Electric Lighting, treated from the Consumer's Standpoint." At present electricity and its varied applications are engrossing public attention to a very large extent, and the book is designed to place before intending users of electrical energy, in language as simple as possible, such matters connected with its production and distribution as will aid them to form more definite views as to their individual needs. The author is Mr. Ed. C. de Segundo, Assoc.M.Inst.C.E.

On Boyer's Method of Determining Nitrogen.—C. Arnold and Conrad Wedemeyer (*Comptes Rendus*, vol. cxiii., p. 503).—The method was designed for the determination of nitric and total nitrogen. The authors pronounce it useless, like the methods of Ruffe and of Hugo Tamm (Guyard).

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—The attention of the Council of the Institute of Chemistry has been directed to Mr. Johnstone's letter to you, which was published in the *CHEMICAL NEWS*, vol. lxi., p. 184, and they regret to find that the leniency which was shown to him in the settlement of the action has been so greatly misconstrued by him. The statements contained in his letter are for the most part either inaccurate or misleading, but the Council are advised that, having regard to the position now taken by Mr. Johnstone, which will not improbably render further legal proceedings necessary, no useful purpose will be served by the continuance of the correspondence.—I am, &c.,

G. H. ROBERTSON,
Registrar to the Institute of Chemistry
of Great Britain and Ireland.

9, Adelphi Terrace, Strand, W.C.,
October 12, 1892.

ADVERTISING CHEMISTS.

To the Editor of the Chemical News.

SIR,—The public is constantly being advised in the advertising columns of the daily and weekly press that members of the Stock Exchange are not allowed to advertise. It is reasonable to conclude, from the absence of advertisements of licensed medical practitioners and solicitors, that the Royal Colleges of Surgeons and Physicians and the Incorporated Law Society impose some similar regulation upon their members.

Would it not benefit the chemical profession if the Institute of Chemistry were also to forbid its members to advertise themselves in the advertisement columns of the lay and technical press, and were to imitate the Stock Exchange in notifying the public of the existence of the regulation?—I am, &c.,

A. G. B.

October 7, 1892

BOGUS "FELLOWSHIPS."

To the Editor of the Chemical News.

SIR,—Some time ago there appeared in the *CHEMICAL NEWS* letters complaining of persons who fraudulently profess to be Fellows of the Royal, the Chemical, and other scientific societies, and who append to their signatures the letters F.R.S. or F.C.S., &c.

A new abuse is now springing up. Certain persons profess to be "Fellows" of societies which are not incorporated either under Royal Charter or Special Act of Parliament, and which have consequently no legal right to issue "Fellowships" at all. I would beg to caution such societies and such persons that they by no means elevate their standing by such tricks.—I am, &c.,

F.C.S.

"A NEW SILVER ORE."

To the Editor of the Chemical News.

SIR,—Your journal of July 22, which has just arrived here, contains an article on "The Recent Discovery of a New Silver Ore," by Mr. H. N. Warren. The discovery is, that the kaolin ore of the Broken Hill mines contains chloride, bromide, and iodide of silver. The presence of all these minerals in this ore was noticed by Professor Liversidge in 1886, and fully described by him at the time (*vide* "Minerals of New South Wales," pp. 39—*et seq.*).

Large specimens of the kaolin ore containing these minerals, all named, were in the Broken Hill exhibit at the London Crystal Palace Mining Exhibition in 1890 (*vide Mining Journal*, Aug., Sept., Oct., 1890). Your contributor also tells us that this kaolin ore containing 7 to 10 per cent of silver was for years regarded as a waste product. Here he has been misinformed. No "travelling mineralogists" were required to inform the managers of the value of this material, and if the kaolin had "remained untouched to the beginning of this year," but very small dividends would have been paid instead of the millions which have been received by the shareholders. The most absurd statement is that the ore has been tried as a material for porcelain.

The nearest manufacturing town to the mine is Adelaide, 350 miles away; porcelain is not made there, but if fireclay were needed for that or any other purpose it could be obtained within twenty miles of the city, and a supply of even the purest fireclay would be quite worthless hundreds of miles away.—I am, &c.,

GEO. J. ROGERS.

Wallaroo Smelting Works,
South Australia, Sept. 5, 1892.

AGRICULTURAL CHEMISTRY.

To the Editor of the Chemical News.

SIR,—With reference to the review of our "Agricultural Chemistry" with which you have favoured us, and in which you are disposed to question our remarks in exaltation of farmyard manure, it occurs to us that those you have quoted apart from the context may not convey our meaning so clearly as might be, hence a few words of explanation seem desirable if you care to insert them.

Farmyard manure, as compared with many artificial manures whose value can hardly be over estimated, is of course, weight for weight, but poor stuff; its merits, however, are only properly represented when considered in connection with the part it plays in the routine of high class farming as mostly practised in this country. We have to consider the enormous quantity necessarily produced in the conversion of various crops into animal produce, and the fact of its being obtained without cost of carriage (which cripples all low class manures), except from one part of the farm to another; and especially the fact that it is the medium and diluent for highly concentrated manurial products obtained from cakes, &c., which form a material element in their value, and the importance of which we have endeavoured to illustrate in our new introductory remarks.

Again, in regard to sewage manures our poor opinion of these refers to manures obtained by precipitation from sewage, as it occurs in the sewers of London and other large towns, where the valuable constituents are diluted with an enormous proportion of water. The instances you mention of manures yielding 3 per cent of ammonia and 5 per cent phosphates could hardly refer to any products obtained on a commercial scale from this source, but probably to excrementitious materials procured without the use of water; of such material, or at least the liquid portion of it, we have spoken most favourably, and referred to it as a neglected source of manurial nitrogen.—I am, &c.,

ALFRED SIBSON.

23, St. Mary Axe, E.C.,
October 8, 1892.

SEWAGE MANURES.

To the Editor of the Chemical News.

SIR,—The sewage manure referred to in our notice of Messrs. Sibson's work on "Agricultural Chemistry" was obtained from water-carried town sewage without any addition of phosphates or nitrogenous matter. But no

lime had been used in their production either in precipitation or during the drying-process. The analyses have been made by competent and disinterested chemists.—I am, &c.,

YOUR REVIEWER.

STILLS AND THE EXCISE.

To the Editor of the Chemical News.

SIR,—Some few months ago I applied to H.M. Commissioners of Inland Revenue, asking for a license to enable me to purchase the old form of methylated spirit (*i.e.*, free from naphtha). My application had the effect of causing my laboratory to be visited by no less than four Government officials, who, during their inspection, discovered that I used stills and retorts for various analytical purposes. I was told that I had no right to use any form of still or retort without paying a license of ten shillings and sixpence, and I was duly served with a notice that I must take out such a license before a certain date. Even Hogg's Patent Still, in which the water is merely condensed against a cold inverted cone, from the apex of which the condensed water drops into a cup and is conveyed outside the apparatus, was considered to be a "still" within the meaning of the Act. Having made enquiries, and finding that very few, if any, chemists paid such a license, I refused to pay, and after a correspondence extending over several months, I have at last obtained, chiefly, I believe, through the efforts of Mr. G. H. Robertson, the secretary of the Institute of Chemistry, the necessary permission to use stills and retorts "for the purposes of my profession." My excuse for troubling you with this letter is, that I believe few analytical chemists are aware that it is necessary to obtain the permission of the Inland Revenue Authorities in order to use ordinary glass retorts and stills.—I am, &c.,

P. GERALD SANFORD, F.I.C.

Laboratory, 20, Cullum St.,
London, E.C.

Determination of Tartar in Sweet Wines, according to the Method of Berthelot and Fleurien.—Dr. E. Ackermann.—In a treatise entitled "Does Every Wine contain Tartar?" Petrowitsch, of Zombor, gave the following figures as the composition of a pure Karlo-witz wine:—

Specific gravity	1.0421
Alcohol (by volume)	14.65
Total acid, calculated as tartaric acid	0.82
Extract	12.65
Sugar	6.76

In the determination of tartar, according to the method of Berthelot and Fleurien, not the smallest trace of tartar was deposited after standing for some days, and he therefore concluded that none was present. There was instead deposited at the bottom of the flask a tough, slimy, brown substance, which the writer considered to be chiefly colouring-matter. Hence Petrowitsch concluded that no tartar was present, but that it had all been precipitated by the alcohol whilst kept in a very cold cellar. Dr. Ackermann obtained a similar deposit from a sweet Greek wine, and found that it consisted chiefly of sugar mixed with tartar. The wine contained 0.8 grm. tartar per litre. Tartar is therefore not necessarily absent in wines containing 14.8 per cent by volume of alcohol. In sweet wines the sugar prevents the crystalline deposition of tartar partially or entirely, according to its quantity. The method of Berthelot and Fleurien is therefore not applicable to sweet wines unless before precipitation they have been thoroughly fermented with a mixture of ether and alcohol.—*Zeit. fur Analytische Chemie*, Vol. xxxi., Part 4.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 13, September 26, 1892.

Suberene, a New Hydrocarbon.—W. Markownikoff.—This compound, on reacting with aluminium bromide, forms a compound, $C_6Br_5CH_3$. Its melting-point is 283° .

Action of Piperidine and Pyridine on the Haloid Salts of Cadmium.—Raoult Varet.—The author has formed and examined the piperidine chlorocadmiate, the A and B bromocadmiates, and the A and B iodocadmiates; as also the pyridine chlorocadmiate, bromocadmiate, and iodocadmiate.

Zeitschrift für Anorganische Chemie.
Vol. xxx., Part 6.

Reaction of Ferric Salts with Soluble Sulphocyanides.—Gerhard Krüss and Hermann Moraht.—Some time ago the authors sought to utilise the spectro-photometric method proposed by K. v. Vierordt for the determination of small quantities of iron, and carry out such determinations, using Vierordt's constant A for the light-absorbing power of iron sulphocyanide. An extended series of experiments showed them that this method led to incorrect results, since the light-obscuring powers of two solutions of iron sulphocyanide for any spectral region is not proportional to the concentration of these solutions. Not merely acids and saline solutions but even water, according to the author's experiments, occasions a dissociation of the red iron compound. A year ago Magnanini (*Rendiconti della R. Accademia dei Lincei*) studied the same iron reaction by means of quantitative spectral analysis, and obtained results which confirm the dissociability of the coloured iron sulphocyanide by water and thus testify against the possibility of a spectrophotometric determination of iron. J. Riban also made a critical repetition of our measurements of the spectrum of iron sulphocyanide and arrived at the same results. As to the analytical phase of the reaction between ferric salts and soluble sulphocyanides, the results of Riban and of the authors seem to contradict the recent observations of M. Lapique. But this contradiction turns on an insufficient distinction between colorimetry and spectro-colorimetry. In a colorimetric manner small quantities of iron may certainly be determined. Thus Mylius and Foerster made use of the sulphocyanide reaction for determining small quantities of iron. It is needful to keep the solutions to be compared in the same stage of dissociation by the addition of equal quantities of sulphocyanide, hydrochloric acid, and water. The authors then proceed to a theoretical explanation of the course of the reaction of soluble sulphocyanides upon ferric salts.

New Process for the Formation of Basic Copper Sulphates.—L. Marchlewski and J. Sachs. If a saturated watery solution of copper sulphate is heated on the water-bath with an excess of the bases dimethylaniline, diethylaniline, and quinoline, the salts formed by the intervention of the two former bases are identical, and correspond to the formula $6CuO, 2SO_3, 5H_2O$, whilst the salt formed in presence of quinoline is $8CuO, 3SO_3, 10H_2O$.

The Quantitative Separation and Determination of Chlorine, Bromine, and Iodine.—Carl Friedheim and R. Jos. Meyer.—The substance of this paper will be given at some length.

A Contribution to a Knowledge of the Complex Inorganic Acids.—F. Kehrman.—A communication from the Inorganic Laboratory of the Technical High

School at Aix la Chapelle. The author examines the phosphotungstic acid with 24 atoms of tungsten, that with 18 atoms, that with 22, those with 21 and with 7, and notices several series of salts which he has obtained but not thoroughly examined. He summarises his investigations as follows. On bringing together tungstates with phosphoric acid or phosphates under different experimental conditions, there ensues the formation of a considerable number of complex salts containing tungstic acid, phosphoric acid, and a base, and being generally hydrated, the acid may in many cases be obtained free, whilst in other salts it is permanent only in combination. If the series of salts thus obtained are subjected under various conditions to the action of acid or alkaline reagents there arise new series of salts by the fissions of the molecules, which again may be further split up by the same means. The number of the compounds already thus obtained or obtainable is very large. But in spite of the great difficulties which the analyses present, the constitution of these puzzling complex acids is possible only by means of a penetrative qualitative and quantitative study of the processes of scission.

Trihaloid Compounds of Rubidium and Potassium.—H. L. Wells and H. L. Wheeler.—The authors have been led to place the trihalogenides in the class of the so-called double halogen compounds. All the potassium compounds can be obtained with identical halogen atoms, whilst in the missing rubidium halogenides the halogen atoms are different.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Monazite.—Messrs. Richard Baker, Son, and Co. will find a description of this mineral and the places where it is found in the "Manual of Mineralogy and Lithology," by Mr. James D. Dana, of New Haven, Connecticut. Messrs. Trübner and Co., of Paternoster House, Charing Cross Road, London, are the publishers of the work.—WILLIAM BROWN.

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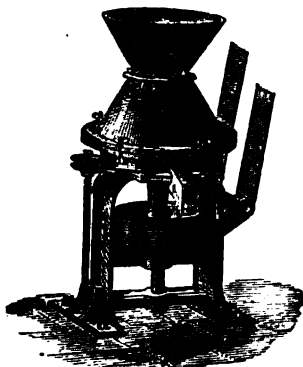
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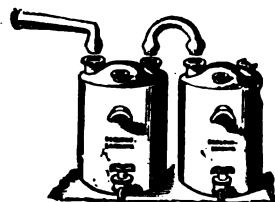
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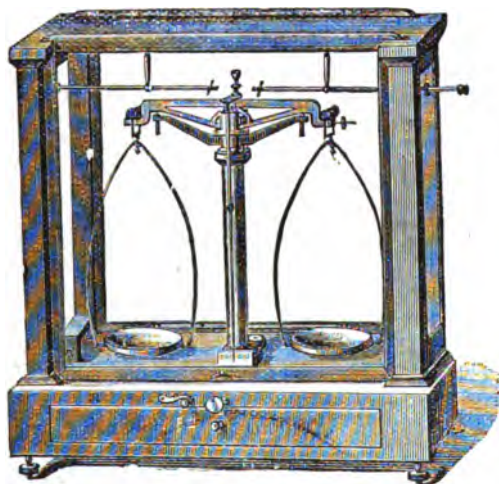


FIG. 36.

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THE CHEMICAL NEWS.

VOL. LXVI., No. 1717.

NOTE ON THE ACTION OF DRY SULPHUR DIOXIDE ON OXY-SALTS.*

By DR. W. R. HODGKINSON, F.R.S.E.,
and J. YOUNG, A.R.S.M.

THE behaviour of sulphur dioxide on solutions of certain oxy-salts, such as nitrates and chlorates, is sufficiently well known, and in fact a matter of everyday occurrence. The reactions of the dry gas on these salts does not, however, appear to have been carefully studied.

Some quantitative experiments have therefore been made with several typical salts. The mode of experiment has been to expose a weighed quantity of the salt to a current of carefully dried SO_2 in a tube so arranged that it could, if necessary, be heated to some definite temperature in an air-bath, or with the naked flame if desired.

Nitrates.—A considerable number of nitrates have been examined. As a rule the action commences at the ordinary temperature, coloured oxides of nitrogen are given off, and when the salt is employed in fine powder the temperature rapidly rises, and the metal in every case is completely converted into sulphate. As long as the materials were quite dry no SO_3 was formed beyond that necessary to form sulphate with the metal. Silver nitrate taken, 1.7068 grm.; sulphate found, 1.5660 grm.; calculated, 1.566 grm. Potassium nitrate taken, 0.9490 grm.; sulphate found, 0.816 grm.; calculated, 0.817 grm.

Chlorates.—The only salts of this class examined were those of barium and potassium. The first result of impact of the SO_2 was the liberation of chlorine peroxide, which escaped along with the excess of SO_2 as long as the temperature did not rise above 60° . At a little higher temperature there was a slight flash in the tube, and formation of white fumes of SO_3 . The escaping gases then contained chlorine, SO_3 , and SO_2 . The yellow but clear mixture of sulphur dioxide and chlorine peroxide became cloudy from formation of SO_3 on introduction of a little moisture. Moist SO_2 appeared to act more rapidly than dry, and in most cases without visible liberation of chlorine peroxide. Barium chloride taken, 0.480 grm.; found as sulphate, 0.364 grm.; calculated, 0.367 grm. Potassium chlorate taken, 1.0982 grm.; found as sulphate, 0.7798 grm.; calculated, 0.7797 grm. Phosphates are apparently not acted upon at all by SO_2 .

With chromates, dichromates, and permanganates considerable differences of behaviour were noticed, depending evidently on the nature of the metal. With silver chromate the figures point to the formation of silver sulphate and chromic oxide. Silver chromate taken, 0.9348 grm.; after heating to near redness weight found was 1.0934 grm.; for a mixture of sulphate with chromic oxide it should be 1.092.

With alkaline chromates, dichromates, or barium chromates there is an evident tendency to form chromium sulphate as well as other sulphate. In no case, however, has the formation of chromium sulphate proceeded its full extent, even when the heating has been continued for many hours in a steady current of SO_2 . Permanganates behave in a similar manner.

With both classes of salts the action is at first rapid during the formation of the more positive sulphate, and ceases at a higher temperature owing to the decomposition of the chromium and manganese sulphates by heat.

	Grms
Potassium bichromate taken	1.6214
After heating in SO_2	2.0256
After re-heating for two hours in SO_2	2.0468
Calculated as a mixture of Cr_2O_3 and K_2SO_4 it would be	1.7945
As a mixture of K_2SO_4 and $\text{Cr}_2(\text{SO}_4)_3$	3.1214
Potassium chromate taken	0.907
After heating for half an hour in SO_2	1.1675
After re-heating for two hours in SO_2	1.2606
Calculated as a mixture of K_2SO_4 and Cr_2O_3 ..	1.1688

The ease with which potassium nitrate was converted into sulphate by the action of dry SO_2 suggested a method for the determination of potassium in gunpowder and similar substances. It was, however, found very unsuitable.

A number of experiments carried out by Lieutenant L. E. Traherne, R.N., show that when gunpowder is acted upon by SO_2 at about 150° , either dry or moist, the temperature rises rapidly, and causes in most cases explosion. With fine-grained powders, and especially when unglazed, the action is more rapid and the explosion violent, as it appears to take place over a considerable area at once.

Chlorates, as might be expected, when simultaneously in contact with SO_2 and any kind of organic matter, set up a violent action. A good form of lecture experiment is to allow one or two drops of a solution of SO_2 in alcohol or ether to fall on a little powdered potassium chlorate; white fumes are given off, which are nearly always followed by a sharp explosion.

ACTION OF AN ELECTRIC CURRENT UPON THE GROWTH OF SEEDS.

By Dr. JAMES LEIOESTER,
Lecturer on Chemistry at the Merchant Venturers'
Technical School, Bristol.

A SHORT note with regard to the above subject has already appeared in the CHEMICAL NEWS: further experiments have been performed with the following results:—

The current has no action, as far as can be observed, upon the growth of plants.

An improvement upon the zinc and copper plates is obtained by using a Daniell's cell; this yields a much stronger current, the current obtained from the plates being only noticeable with the aid of a mirror galvanometer.

Lettuce seeds are the best to illustrate the quicker growth. It appears that the current only acts until the initial store of food in the seed has been used up.

Whether a stronger current than we have so far used would in some way bring the plant food quicker remains to be tried.

NOTE ON THE REICHERT PROCESS FOR BUTTER AND OTHER FATS.

By J. ARTHUR WILSON.

THE Reichert process, which to-day stands in the front of any single method for the analysis of butter-fat, has since its introduction undergone very considerable change, due to the united experience of chemists in all parts of the world. The most noticeable improvements have been those of Meissel, Allen, and, lastly, of Woolny, who, in an elaborate paper (translated in the *Analyst*, xii., 201) has studied the errors and imperfections of the process, and who has formulated a method of working which, if properly carried out, gives the best possible results.

* Read before the British Association Edinburgh Meeting, 1892

Richmond (*Analyst*, xvii., No. 197) has reviewed the history of this process and its modifications, especially with regard to the limit of various observers. There is one point which seems to have occupied notice, namely, the increased rate of distillation of volatile acids, with increase of salts in solution. This was observed long ago by myself in the case of acetic acid, and the effects of varying proportions of salts of the alkalis, especially, determined (see the *Four. Soc. Chem. Ind.*, x., No. 1). It is therefore very necessary that in all such determinations as the Reichert or Woolny value the same quantity of alkalis and acids must be employed; otherwise, exact agreement between two operators will be impossible. If sodium hydrate be used in place of potassium hydrate, as in the Woolny process, then there will not be the agreement one might expect. The same remark applies to the substitution of oxalic acid or phosphoric acid for the sulphuric acid usually employed for liberating the fatty acids.

The exact determination of the influence of salts on the process as carried out in actual practice would be interesting and valuable.

Tottington Mills, October 3, 1892.

ON THE DETERMINATION OF WATER AND OF FREE FATTY MATTER IN SOAP.

By J. ARTHUR WILSON.

THE usual method of determining water in soap by drying a weighed quantity of the sample, cut into thin shavings, at increasing temperatures up to 110° C., does not give the most accurate results, and, besides, is frequently very tedious. Watson Smith's modification has in my hands not been successful, especially with highly watered soaps. The free fatty matter is also very frequently considerably in error when done by the old process, especially when extraction is continued for only four hours.

By the methods to be now described, the time required for both determinations is materially shortened and greater accuracy obtained.

Water Determination.

About 25 grms. of the sample is weighed out in a thin flat-bottomed porcelain dish, 3 inches diameter and 0.5 inch deep (such as are used for total solids in milk analysis). It is gently melted, and 5 c.c. of absolute alcohol added, and the dish warmed on the water-bath till soap is dissolved; whereupon about 10 grms. of ignited sand is added and incorporated with the dissolved soap: the dish is afterwards placed on the water-bath for one hour. 5 c.c. of absolute alcohol is then poured over the sand, then the dish is placed in the air-bath at 100–105° C. till constant weight is attained. With ordinary soaps, and the use of the improved air-bath, this will be in about three hours; whilst highly watered soaps require about five or six hours.

Determination of Free Fat.

The residue from the water determination is ground up in a glass mortar, and transferred to the Soxhlet tube, and exhausted with re-distilled petroleum ether; two hours being sufficient under these conditions. The Soxhlet tube should have a mercury seal and ground joints in place of corks.

Modifications.

If the sample contains free caustic alkali (easily seen by dropping a little phenolphthalein on a clean surface of the sample), the residue from the water determination cannot be used for the determination of the free fat, on account of the saponification of the latter by the free alkali. In such a case, the ordinary method of determining the

water is adopted, but it is not necessary to prolong the drying more than four hours. The dry residue is then ground up with 10 grms. of sand, transferred to the Soxhlet, and exhausted as before.

The improved process for free fat determination gives higher results for the same reason that the paper coil and plaster processes do in milk analysis.

Tottington Mills, October 6, 1892.

THE CONDITIONS OF THE FORMATION AND DECOMPOSITION OF NITROUS ACID.*

By V. H. VELEY, M.A.

(Continued from p. 191).

Summary of Results.

I. The reaction between nitric oxide and nitric acid varies with the concentration of the acid and the temperature; with more concentrated acids nitrogen peroxide is at first formed and then nitrous acids; with less concentrated acids the latter is produced at once.

II. Only with quite dilute acids (of 30 per cent concentration and below) does the reaction between the nitric oxide and nitric acid appear to be reversible; the average value for $p/q = 9$ (p = quantity of nitric, q of nitrous, acid), though the actual value varies from 3 to 4 per cent on either side according to the conditions of the experiment.

III. With more dilute acids the amount of nitrous acid formed increases slightly and then decreases with the temperature; but with more concentrated acids the amount uniformly decreases.

IV. The proportional quantity of nitrous acid formed increases with decrease of concentration, but the actual quantity is of course less.

It would appear that the simple reversible reaction between nitric oxide and nitric acid becomes modified with acids above a concentration of about 30 per cent and a temperature of 32°. These were also approximately the limits of concentration and temperature, above which the reactions between metals and nitric acid could not be prevented by substances such as urea, potassium chlorate, and the like. I will, however, merely allude to the point without wishing to lay an undue stress upon possibly nothing but chance coincidences.

The Rate of Decomposition of Nitrous Acid.

The velocity of the decomposition of nitrous acid, presumably in nitric acid solution, has been made the subject of a previous investigation by Clemente Montemartini (*vide supra*). As a result of several series of experiments this writer considers that the rate of this decomposition may be expressed by the differential equation—

$$(I). \frac{dC}{dT} = kC \quad \text{or} \quad (II). k = \frac{1}{T} \log \frac{C_0}{C_1},$$

in which C is the concentration, T the time, and k is a constant.

This equation will be discussed in the sequel. My experiments were commenced primarily with a view of ascertaining if nitrous acid is the more stable the greater the proportion of nitric acid present, a point which was raised in the course of my investigations on the reactions of nitric acid and metals. Further, it seemed probable that the presence of metallic salts might also affect the stability of nitrous acid, as Armstrong and Acworth (*Chem. Soc. Journ.*, 1877, ii., p. 54) allude to the persistence with which the nitrous acid is retained by solutions containing the products of the reaction between nitric acid and metals. It also seemed possible that such a line of inquiry might throw some light upon the nature of an acid intermediate between nitrous and nitric acids, in

* A Paper read before the Royal Society, June 2, 1892.

whose existence certain writers believe, though the facts adduced at present are perhaps hardly sufficient to warrant such a belief.

The apparatus and method of experiment finally adopted were as follows:—The nitrous acid solution was placed in a cylindrical tube containing 100 c.c. up to a certain mark; at its upper end were two apertures, into one of which was sealed a glass delivery tube, while the other could be wholly or partially closed by a small rubber plug through which passed a pipette of exactly 2 c.c. capacity. The former, which served for the passage of a stream of carbonic acid, was sealed off at its lower end, the gas passing through a small pinhole at the side, and thus not directly impinging upon the liquid; the space between the loosely-fitting plug and the glass wall serving for its exit. At the end of certain intervals of time the plug was rammed in, whereby the pressure of the gas forced the liquid up the pipette: when this was filled up to the graduation mark the sample was removed for analysis, while the aperture of the cylindrical tube was partly closed meanwhile by a duplicate plug. The cylinder was immersed in a water-bath, the temperature of which was kept constant to within one-tenth of a degree on either side of that required. Before any observations were made the ratio of nitrous to nitric acid present was determined.

Nitrous Acid from Silver Nitrite and Hydrochloric Acid.

The solution of nitrous acid was prepared in the usual manner by the decomposition of re-crystallised silver nitrite with a slight deficiency of hydrochloric acid, and the liquid filtered from the precipitated silver chloride into the decomposition flask. The amount of nitrous acid was determined at the end of fixed intervals of time, generally half an hour, and the results calculated on the hypothesis that the volume of the liquid was maintained constant throughout the course of the experiment.

In the following Table the results obtained are set forth, in which T is the time from start and C the concentration of the solution.

SERIES XXIII.

Volume of solution = 60 c.c. Temperature, $24.9^{\circ} \pm 0.1$.
Ratio of nitrous to nitric acid = 1:3.86.

T.	C.	T.	C.
	Grm.		Grm.
0	0.3063	120	0.2306
30	0.2793	150	0.2130
60	0.2559	180	0.2017
90	0.2413	210	0.1890

These results are expressible by the formula—

$$\log(T+t) + \log C = \log k,$$

in which T is the time from start, and t an interval of time which would have elapsed from the moment at which, conditions remaining otherwise the same, the amount of nitrous acid was infinitely great, namely, $C = \infty$, and that moment at which the experiment was actually commenced, C is the concentration, and k is a constant.

In the above series the value for t is taken as 320', and in the Table below are given the values for $\log(T+t)$, $\log c$, and $\log k$.

Log (T+t).	Log C.	Log k.
2.5051	1.4861	1.9912
2.5441	1.4461	1.9902
2.5798	1.4080	1.9878
2.6128	1.3825	1.9953
2.6335	1.3629	1.9964
2.6627	1.3283	1.9910
2.6901	1.3046	1.9947
2.7160	1.2764	1.9924

The values in the third column show great concordance; if the mean 1.992 be taken and the results calcu-

lated therefrom, the observed and calculated values for the concentration of the nitrous acid will compare as follows:—

C (observed).	C (calculated).	C (observed).	C (calculated).
Grm.	Grm.	Grm.	Grm.
0.3063	0.3071	0.2306	0.2285
0.2793	0.2808	0.2130	0.2138
0.2559	0.2586	0.2017	0.2006
0.2413	0.2397	0.1890	0.1890

The greatest difference occurs in the third value, which is rather less than 2 per cent, which can readily be accounted for by errors of experiment in dealing with a substance so susceptible of decomposition as nitrous acid. The curve which represents the concentration of the acid in terms of time is a portion of a hyperbola, the differential equation of which is—

$$\frac{dC}{dT} = -\frac{C^2}{M},$$

which expresses the rate at which equivalent masses react, whether it be of the nitric with the nitrous acid, or the nitrous acid with itself; in each experiment $1/M$ is the amount of each unit mass which reacts with the other per unit time when an unit mass of each substance is present.

(To be continued.)

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1892.

By WILLIAM CROOKES, F.R.S.,

and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, October 10th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from September 1st to September 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined, the whole were found to be perfectly clear, bright, and well filtered, the somewhat considerable rainfall on the 21st and 22nd September, amounting at Oxford to 0.76 of an inch, being without obvious effect on the subsequent supply. There was also a fall of 0.71 of an inch on the last day of the month.

In respect to the smallness of the proportion of organic matter present, the character of the water furnished by the seven companies continued to be entirely satisfactory, the mean amount of organic carbon in the Thames-derived supply, for example, being 0.118 part, and the maximum amount in any single sample examined being but 0.145 part, in 100,000 parts of the water—numbers practically identical with those of the previous month, or

0.115 part for the mean and 1.52 part for the maximum amount.

As observed in previous reports, so long as the amount of organic matter in the water supply, as estimated alike by the combustion and oxidation processes, continues absolutely small, the seasonal variations in amount are of no practical significance. With the coming on of autumn and winter, however, it is not to be expected that the low average of the past six months will be much longer sustained; this average, in the case of the Thames-derived supply, amounting only to 0.116 part of organic carbon in 100,000 parts of the water, with a maximum, twice met with, of 0.152 part in any individual sample. It is to be noted that the water supply to London is habitually at its best during the hot season, when a high quality of the supply is more especially called for.

We are, Sir,
Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.

ON THE REACTIONS OF FERRIC SALTS WITH SULPHOCYANATES.

By H. M. VERNON, B.A.

(Continued from p. 193).

IN solutions containing one hundred equivalents of ferric citrate the colour due to the ferric sulphocyanate formed was so much masked by the yellowish brown colour of the citrate that no proper measurements could be made. It was not possible to allow for the colour effect due to the citrate, as its colour was so totally different from that of ferric sulphocyanate. It was not possible in most cases to determine the colour effects of barium sulphocyanate with ferric salts, as precipitates were formed. This was the case even in the equal equivalent solutions. Also, the colour reactions of sulphocyanates with ferric oxalate could not be determined, as the large quantity of free oxalic acid, which must be present to keep in solution the ferric oxalate, decomposes almost all the ferric sulphocyanate, so that the colour effect produced is too small for accurate measurement.

With solutions containing equivalent quantities of ferric salt and sulphocyanate, the colour constants show a general similarity to the constants for the former series, but they differ from them in several respects. Thus the constants for ferric nitrate are considerably larger than those for ferric chloride, whilst in the former series they are only slightly larger. The constants for ferric sulphate are slightly greater than before, but whilst those for ferric acetate are also larger, those for the tartrate are considerably smaller. In the paper before alluded to the author showed that ferric tartrate decomposed greatly in dilute solutions, with formation of ferric oxide. It is to this that the small colour constants for ferric tartrate are due. In the 100 equivalent solution at 160 litres dilution the solution of the salt is moderately concentrated, and therefore but little of it is decomposed; but in this solution at 800 litres dilution, and in the equal equivalent solutions where it is more dilute, the colour constant is not much more than half what it should be, as the portion of the tartrate decomposed no longer reacts with it. The colour values for ferric tartrate, citrate, and acetate solutions at 160 litres dilution were so small that they could not be determined with any approach to accuracy. They are accordingly omitted from the Table.

With solutions containing 100 equivalents of ferric chloride the colour constants for the various sulphocyanates decrease to very nearly the same extent on dilution from 160 litres to 800 litres as for potassium sulphocyanate; and as the proportion of ferric sulphocyanate in these solutions decrease on dilution according to the law of

mass, the law holds with the other sulphocyanate solutions. As the colour constants for ferric nitrate do not vary on dilution, the ferric sulphocyanate in solutions of ferric nitrate and sulphocyanates is also affected by dilution in accordance with the law of mass. With ferric sulphate solutions, however, the colour decreases at a greater rate than in accordance with the law, as is shown by the decrease in the colour constants at 800 litres dilution.

An explanation has already been afforded of this, and also of the abnormally great decrease of colour of ferric tartrate solutions on dilution. The colour decrease of ferric acetate solutions is due to the same cause as that of the tartrate solutions, for ferric acetate solutions are also largely decomposed on dilution, with formation of free ferric oxide.

Solutions containing equal equivalents of ferric chloride or nitrate and the various sulphocyanates appear to obey the law of mass moderately well. Those for ferric sulphate show great irregularities, the colour constant seeming to decrease at 80 litres dilution and to increase again on further dilution. Ferric citrate and acetate solutions also show slightly greater constants at 80 litres than at 40 litres dilution. Taken as a whole, the numbers for equal equivalent solutions show much greater irregularities than those for solutions containing 100 equivalents of ferric salt, and they are evidently not nearly so trustworthy. With 100 equivalent solutions many of the errors which are very large with equal equivalent solutions dwindle down to insignificance. Thus the amount of ferric sulphocyanate formed does not vary much with dilution, and would indeed be little greater at infinite concentration, the point at which the colour values should be theoretically determined, than at 160 litres dilution. With equal equivalent solutions it has been shown that the colour value at 40 litres is only about a fourth its value at infinite concentration, and as it is not known for certain whether the amount of ferric sulphocyanate in the various solutions varies with the dilution according to the law of mass, the colour values found may be far from proportional to the true value at infinite concentration. Again, there is not so much likelihood of the formation of basic salts, and if such were formed, not nearly so much error would be introduced as with equal equivalent solutions, in which the removal of a part of the ferric salt in this way would mean the non-formation of a corresponding amount of ferric sulphocyanate.

With regard to the nature of the colour constants of the various ferric salts and sulphocyanates, it is evident that they must depend on the relative affinities of the various acids and bases reacting in the solution. Thus, in a solution of ferric chloride and potassium sulphocyanate there are also present ferric sulphocyanate and potassium chloride, and the amount of ferric sulphocyanate formed depends, on the one hand, on the relative affinities of hydrochloric acid and sulphocyanic acid for ferric oxide, and, on the other hand, on the relative affinities of these acids for potash.

In the Table are given the colour constants of the various acids the ferric salts of which were used, and of the various bases the sulphocyanates of which were used. The means of the numbers are given for 100 equivalent solutions for 160 litres dilution, and the means of the numbers for all three dilutions. The means of the numbers for all the dilutions for equal equivalent solutions are also given. The colour constants of hydrochloric acid and of potash are taken as 100, and the other values compared against these. The coefficients of affinity, as determined by electro-chemical methods (Ostwald, *Lehrbuch*, ii., 823 and 839) are given, and also those of the acids as determined by saponification of methyl acetate (Ostwald, *Lehrbuch*, ii., 803) and of the bases by saponification of ethyl acetate (R. Warder, *Amer. Chem. Journ.*, 1882).

There are considerable resemblances between the colour constants of the acids examined and the electrical conductivities. If the colour constants for 100 equivalent solutions at 160 litres dilution—which are un-

Acid or base.	Means of constants for 100 equivalent solutions at 100 litres dilution.	Means of constants for 100 equivalent solutions at all dilutions.	Means of constants for equal equivalent solutions.	Electrical conductivities.	Velocity constants as shown by saponification of methyl and ethyl acetate.
Hydrochloric	100	100	100	100	100
Nitric	101.7	103.5	115.4	99.6	92
Sulphuric ..	66.2	62.2	69.7	65.1	73.9
Tartaric ..	41.5	33.7	26.5	2.28	2.30
Citric	—	—	22.6	1.66	1.63
Acetic	18.8	16.6	21.8	1.424	0.345
Potash	100	100	100	149	2.298
Ammonia ..	92.4	91.9	80.8	4.8	0.011
Soda	84.9	86.1	69.7	161	2.307
Lithia	58.1	55.7	39.0	142	—
Lime	70.9	69.1	63.9	—	2.285
Baryta	73.8	71.9	55.8	—	2.144

doubtedly the most trustworthy—be compared with the electrical conductivities, the values for sulphuric acid, compared with those for hydrochloric acid, differ by less than a unit. The conductivity of nitric acid is slightly smaller than that of hydrochloric acid, whilst with the colour constants the reverse is the case. The difference is, however, within the limits of experimental error, as even the electrical conductivity values are liable to an error of two or three per cent or more. Though the colour constants of tartaric, citric, and acetic acids are considerably smaller than those of the other acids; and though they are of the same order as the electrical conductivities, that of tartaric acid being most, and of acetic acid least, yet they bear no numerical resemblance to them. The value for tartaric acid is eighteen times as large as the conductivity, and that of acetic acid thirteen times as large. The colour constant for citric acid could not be determined for 100 equivalent solutions, but the constants for equal equivalent solutions show that it lies between the numbers for tartaric acid and acetic acid, as its conductivity does.

It is thus evident that there is a considerable general resemblance between the colour constants and the conductivities of the acids examined, even if there is not a numerical one. The colour constants for the bases show scarcely any resemblance to the conductivities. Thus soda has a greater conductivity than potash; its colour constant is considerably less. The conductivity of ammonia is not a thirtieth that of soda; its colour constant lies between those of potash and soda. The colour constant of lithia is considerably smaller than those of soda and potash; but its conductivity, though smaller than those of soda and potash, does not differ from them much. The colour constants for lime and baryta are nearly equal, and are slightly smaller than the value for soda. This is the sole resemblance between these numbers and the affinity coefficients; for the velocity constants of lime and baryta are also similar, and slightly smaller than the value for soda. Why the colour constants for the bases should exhibit such slight resemblance to the conductivities, when for the acids there is considerable similarity, it is not possible to say. If determinations of the colour constants of solutions containing 100 equivalents of sulphocyanate could have been properly carried out, a greater resemblance might perhaps have been found to exist.

Whatever resemblance or otherwise the colour constants of the acids and bases examined bear to their affinity coefficients, it is nevertheless evident that the amount of ferric sulphocyanate formed in a solution containing a ferric salt and a sulphocyanate is proportional to the product of two numbers, one depending on the nature of the acid and the other on the nature of the base. It is not in any way possible to express the amount of ferric sulphocyanate produced in the form of a sum of

two quantities. This rule, found to obey for ferric salts and sulphocyanates, must hold for all salt solutions, so that when any two salts are mixed in a solution it follows that, no precipitate being formed or no product being otherwise removed from the solution, the quantities of the fresh salts formed by their interaction are proportional to the product of two constants. The quantities of the original salt still remaining of course depend on a similar rule. The final proportions of the salts formed depend on a balance between these two contrary reactions. The salts are probably formed according to the same rule, whether they are partially or wholly dissociated in solution or not.

(To be continued).

THE USE OF FLUORIDES IN THE MANUFACTURE OF ALCOHOL.*

By Dr. LEO BAEKELAND.

DR. EFFRONT'S researches on the antiseptic properties of fluoride compounds have lately received important applications in the alcohol industry, and a condensed statement upon this subject may be of interest not only to alcohol manufacturers, but also to the biological chemist.

It is a known fact that for the transformation of starch into maltose and dextrin by the action of diastase, the most favourable temperature is from 50 to 60° C. At any lower temperature the action of the diastase becomes slower, while a higher temperature has a destructive effect upon this soluble ferment, which at 80° C. completely loses its saccharifying power.

In laboratory experiments where pure starch and pure diastase can be used it is possible to exclude all secondary influences from other ferments. In practice, however, conditions are far different; the raw materials (malt, grain, corn, potatoes, &c.), introduce other ferments which have a very disturbing influence. Already during the germination of the grain we notice that besides the useful diastase, a certain quantity of organic acid is developed. But this is only the beginning of the trouble, for we see this acidity increasing during all the following operations, from the making of the sweet wort to the end of the alcoholic fermentation. This acidity is due chiefly to the formation of lactic and butyric acids, which are the result of the activity of well specified micro-organisms, the lactic and butyric ferments, the latter being more specially known as *Clotridium Cutyricum*. If a small quantity of lactic acid seems to be favourable to a healthy development of yeast cells, a too large quantity of this acid is useless if not harmful, and any quantity of butyric acid is decidedly injurious to the enzymatic action of the diastase as well as to the alcoholic fermentation.

Alcohol manufacturers are very cautious to avoid acidification, as they know that the yield of alcohol is smaller in proportion to the increasing acidity of their wort or mash.

The ferments which develop these acids are particularly active at a temperature of from 50° to 60° C. This means that just that temperature which is most favourable for the diastatic action of the malt will also allow the acid ferments to show their harmful action and to develop the largest quantity of lactic and butyric acid. At a higher temperature, however, the action of butyric and lactic ferments is paralysed, and this is the reason why in making sweet wort a temperature is selected whereby the development of acidity is retarded, and by which the diastase does not lose too much of its power. But this means a loss of malt on account of the weakening of the power of the diastase contained in it.

The injurious action of this higher temperature on the diastase is not limited to this; facts have proven that

diastase which has been submitted to a higher temperature, if only for a moment, has been irremediably injured in regard to its future properties; it will not keep its enzymotic action as long as it would if it had been kept in healthy conditions. This fact is very important if we recollect that the saccharification of the wort is never complete, and that the diastase is expected to continue its action during the whole period of alcoholic fermentation in order to saccharify the last quantities of starch left in the wort. Other means have been tried in order to combat the butyric and lactic bacilli, and the use of sulphuric and muriatic acid, sulphites, and other antiseptics have been proposed. None of them has proved of great advantage; they all show an injurious effect upon the diastatic action of the malt, and the activity of the alcohol ferment.

Hydrofluoric acid or soluble fluorides, on the contrary, when used in very small doses, prevent the development of butyric and lactic acid and are completely harmless to the diastase or to the alcoholic ferment. Furthermore, such small quantities of fluoride, instead of injuring the diastase, seem to excite its activity and preserve its power for quite a longer period than when used alone. Experiments have shown that by addition of a small quantity of fluoride, diastase could be kept in action during seven days, and at the end of this period 80 per cent of the original quantity of diastase was still active, while without the use of fluorides the quantity of active diastase is reduced to 12 per cent at the end of the same period.

No other antiseptics or mineral acids show these preserving qualities when added to diastase. Mineral acids, for instance, when used even in very moderate quantities, have killed the whole of the diastase after five days.

A first advantage of the use of small quantities of fluorides is thus to save malt, of which less need be brought in operation, still giving the same result as larger quantities when used without fluorides. This malt will have a more free and more complete action, and this action will be continued for a longer time on account of the antiseptic properties of fluorides, development of organic acids will be prevented, and the wort can be kept nearer between 50° and 60° C., which is the temperature at which diastase is most active, and where its enzymotic powers are best kept up.

The addition of fluorides have rendered possible the use of malt of very inferior quality with surprising results.

The same beneficial effect of hydrofluoric acid or its salts is observed during the alcoholic fermentation, which thereby becomes more regular and more complete.

The fermentation keeps up with about the same intensity during the whole period until all the saccharine matter has been converted into alcohol. The liquid finally proves to be far less acid than if no fluoride is used. The practical result of all this is a larger yield of alcohol and a better product. If small quantities of fluoride have a beneficial effect on diastase and alcoholic ferment, the contrary result is obtained if larger quantities of fluorine compounds are used. An addition of 25 grms. of commercial hydrofluoric acid (30 per cent) per hectolitre of wort proved very injurious to the action of the diastase, even at temperatures as low as 30° C. At higher temperatures, 55° C. for instance, this injurious effect was already produced by 6 or 7 grms. of hydrofluoric acid per hectolitre. Very concentrated or very acid worts have proved especially sensitive to large quantities of hydrofluoric acid.

The same bad effects of an excess of hydrofluoric acid are shown in the alcoholic fermentation which in some cases may be entirely stopped by it. Soluble fluorides, however, even when used a little in excess, are less violent in regard to this. All this shows that if we have in fluorides a sure and powerful destroyer of useless ferments, this agent should be used judiciously, as any excess of it may prove detrimental to the expected results.

It would be out of the question to give a general recipe

for the quantities of hydrofluoric acid or fluorides which should be used; this depends on too many conditions, such as quality of material, temperature of mashing, concentration or acidity of the wort. For instance, quantities of fluoride which may be advantageous in a wort of average concentration and at a low temperature may become injurious in a more concentrated wort, or if kept at a higher temperature.

In every instance where the fluoride process is introduced in a distillery, some preliminary testing has to be done in regard to this before the best effects are obtained.

The destructive action of fluorides on butyric bacilli in the mash can be easily observed by the aid of the microscope. (See "Das Flusssäure Verfahren in die Spiritus-fabrikation," by Dr. Maerker. Berlin: Verlag von Paul Parey).

The chemical effect of fluorides is better demonstrated by the following experiment (See Soxhlet, *Zeitschrift des Landwirths-Vereins in Bayern*, July, 1890):—1000 grms. of crushed corn were boiled with four litres water and the resulting starch heated in a digester (autoclave) at 3 atm. pressure during one hour. The resulting liquid was cooled off to 50° C., and then 80 grms. of dry malt were added, and the saccharification kept on at this temperature for about thirty minutes. The resulting sweet wort was divided into two equal portions. To one portion 150 m.grms. of ammonium fluoride were added (corresponding to 6 grms. per hectolitre) and the other portion was left as it was. Both portions were kept constantly at 30° C. After two days, the wort without fluoride had considerably thickened and was full of gas bubbles, while the other portion which contained fluoride remained entirely clear and liquid.

A comparative analytical examination of both liquids showed:—

	No fluoride.	Fluoride.
Degrees saccharometer	13.30	13.60
Maltose	10.12	11.61
Dextrin	2.07	1.07
Acidity (normal soda solution per 100 c.c. wort)	8.15	3.9

(To be continued).

ON THE MANUFACTURE OF ALKALINE NITRITES, LEAVING WHITE-LEAD AS A BY-PRODUCT.

By H. N. WARREN, Research Analyst.

THE production of sodium nitrite, which is at present being extensively used as a reducing agent in the arts and manufactures, has of late become the subject of no small amount of research in order to obtain a product of uniform percentage, and at the same time possessing marketable appearance.

The history of white-lead has also been so extensively dealt with in the previous pages of scientific literature that, in order to deal more fully with the subject, or at least in a beneficial manner, presents at once a problem that can only be solved with difficulty.

Sodium nitrite of 98 per cent is at the present time realising £30 per ton, and white-lead £20, but to manufacture these compounds up to the above percentage by any of the ordinary methods, entails considerable expenditure as regards the depreciation of plant, &c., leaving little room for profit; and to avoid these difficulties the author has contrived a method by which galena is caused to act as a reducing agent upon sodium nitrate, yielding at the termination of the reaction sodium nitrite, sodium sulphate, and white-lead. The process, as briefly detailed, is brought about as follows:—

A sufficiency of commercial nitrate is intimately mixed with a sufficiency of ground galena, to which is supplied

an adequate portion of water, and the whole introduced into a capacious leaden retort, after which is added a sufficiency of vitriol. The reaction which is thus afforded terminates with the production of sulphate of lead which remains in the retort; while at the same time the nitrous gases thus freed by the liberated nitric acid coming into contact with the galena are ejected from the retort by blowing in a current of air, and conveyed hence into a solution of soda-ash, thus causing a free evolution of carbonic acid; whilst sodium nitrite remains in solution and requires merely crystallising to render it saleable. The sulphate of lead remaining is next treated with a solution of sodium carbonate and sodium hydrate, and boiled in contact with the same until completely converted into white-lead, requiring only to be dried. As expected, the first samples of white-lead thus produced were entirely useless, presenting no body, and of a very inferior colour; but after a considerable lapse of time, the author has had the satisfaction of preparing by the introduction of certain ingredients not hitherto noted a compound possessed of properties corresponding to the finest prepared Dutch samples, and rivalling the same as regards colour.

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NEW METHODS FOR QUANTITATIVE ANALYSIS.*

By A. BAUMANN.

(Continued from p. 194).

Determination of Lead.

THE decomposition of chromic acid with hydrogen peroxide may also be utilised for the determination of lead, bismuth, and barium,—elements which form with chromic acid compounds insoluble in water. The experiments required have been executed by A. Baumann and G. Hauck.

For the determination of lead the solution is first mixed with sodium acetate, partly to remove any free nitric acid which may be present, and partly to neutralise the acid liberated in the subsequent treatment with chromic acid. The quantity of the sodium acetate to be added depends on the quantity of free acids present. In most cases from 1—2 grms. will be sufficient, but even a large excess of sodium acetate does not endanger the accuracy of the determination.

The liquid is heated to ebullition, and a solution of potassium bichromate is gradually added until the liquid floating above the precipitate is distinctly yellow. Too large an excess of the bichromate is to be avoided. The lead chromate is filtered off and washed with water. The filter is then spread out upon a small glass plate and the precipitate is rinsed with dilute sulphuric acid (applied with a washing-bottle) from the filter directly into the wider space of the gas-generator. From 5 to 6 c.c. of 2 per cent hydrogen peroxide are then introduced into the small glass cylinder of this vessel; the generating vessel is connected with the gas-meter, the two liquids are mixed and shaken in the manner already described after the temperature has become equalised.

The volume of oxygen read off is reduced to 0°, and 760 m.m. atmospheric pressure, and the resulting number is multiplied by 4.9776. The weight of lead oxide sought for is thus obtained in m.grms; for 1 c.c. oxygen equals 4.9776 m.grms. PbO (the atomic weight of Pb = 206.4).

As 1 mol. chromic acid, CrO₃, combines with 1 mol. lead oxide to form lead chromate, and as a mol. chromic acid with hydrogen peroxide evolves 4 atoms of oxygen, 4 atoms of oxygen liberated indicate 1 mol. lead oxide, i.e., 4 × 15.96 parts by weight of oxygen = 222.36 parts

by weight of lead oxide. Thus we obtain the number 4.9776 on the supposition that 1 c.c. of oxygen weighs 1.42908 m.grms.

As it will be seen the gas-volumetric determination of lead depends mainly on the liability of lead chromate to be decomposed by an excess of free dilute sulphuric acid, with formation of lead sulphate, and free chromic acid, which then, with hydrogen peroxide, evolves the quantity of gas corresponding to 4 atoms of oxygen.

It must be mentioned that this decomposition of lead chromate only takes place with the desirable rapidity if the quantity of the precipitate of lead is small. With larger quantities (200 m.grms. lead chromate or upwards) it is well to digest the lead chromate for several hours with dilute sulphuric acid before the volume of the gas is measured. Otherwise in the determination it is necessary to shake for fifteen to twenty minutes until the analysis is complete.

Lead may be determined more simply and quickly by difference with any solution of potassium bichromate (the standard of which may be very quickly ascertained by a gas-volumetric determination), than in the direct manner. The indirect method is therefore to be especially recommended when several analyses have to be executed in succession, or when considerable quantities of lead have to be determined in a liquid.

For effecting the indirect analysis the plumbiferous liquid, which must contain only very little nitric acid in excess, is introduced into a measuring flask containing 100 c.c., diluted with water to about 50 c.c.; sodium acetate is added (about 1 gm.), and it is precipitated in heat with a quantity of potassium bichromate of known strength, very accurately measured with a pipette, so that the supernatant liquid may appear distinctly yellow. It is then allowed to cool, filled up to the mark, filtered through a dry folded filter, and from 30 to 50 c.c., after the addition of 10 c.c. of dilute sulphuric acid, are taken for the gas-volumetric determination. The results obtained by both methods are very accurate.

5. *Determination of Bismuth.*—For the gas-volumetric determination of bismuth the orange-red bismuth chromate, (BiO)₂Cr₂O₇, is most suitable. It is obtained by pouring a solution of bismuth nitrate, as neutral as possible, into a hot solution of potassium bichromate.

The bismuthiferous liquid, which must not contain more than very minute quantities of free nitric acid, must be poured, whilst constantly stirring, into a hot solution of potassium bichromate, taking care that the bichromate remains in slight excess. The precipitate must be throughout of an orange-yellow, and so dense that the supernatant reddish yellow liquid becomes very quickly clear. If the precipitate has more of a yolk of egg colour, a little more of the bichromate solution must be added. The whole is then boiled for about ten minutes, or placed in a boiling water-bath; the precipitate, which deposits rapidly, is washed with hot water by boiling and decantation. Hereupon the bismuth chromate is re-dissolved in a little dilute hydrochloric acid, and the solution is rinsed into the wider space of the gas-generating apparatus. The portions of precipitate which adhere to the filter are easily washed into the generator with dilute hydrochloric acid (as in the determination of lead). Ten c.c. of dilute sulphuric acid (1:5) are added to the chromate solution, from 5 to 10 c.c. of hydrogen peroxide are put into the small glass cylinder, and the chromic acid is determined gas-volumetrically by mixing and shaking the liquids.

As according to the above formula, which may also be written 2CrO₃.Bi₂O₃, 2 mols. of chromic acid come to 1 mol. bismuth oxide, and as the former with hydrogen peroxide yield 8 atoms of oxygen, 8 × 15.96 parts by weight of oxygen = 463.88 parts by weight of bismuth oxide (atomic weight of Bi = 208). Hence it is calculated that 1 c.c. of oxygen evolved at 0° and 760 m.m. barometric pressure represents 5.192 m.grm. bismuth oxide.

In order to find from the volume of oxygen read off the

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quantity of bismuth in m.grms., we reduce the volume to 0° and 760 m.m. pressure, and multiply the number obtained with 5.192.

The determination of bismuth, like that of lead, may also be effected indirectly, the bismuth being precipitated in the manner described with a measured excess of bichromate solution of known strength in a 100 c.c. flask, filling up to the mark and determining the chromic acid in a part of the filtrate. The indirect method is more convenient and quicker, as it requires no care in filtering the precipitate, and the washing is dispensed with.

(To be continued.)

THE LAWS AND NATURE OF COHESION.

PART I.

By REGINALD A. FESSENDEN,
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DESIROUS of finding some relation between the conductivity of metals and their other physical properties, the writer several years ago began to tabulate all the data he could find. Realising the uselessness of comparing the properties of substances whose natures are essentially different, as wood and iron, it was decided to confine the work to the elementary substances. It was found that the only elements whose properties were at all well known were those of the five chemical groups comprising the following metals:—(I.) iron, nickel, cobalt, platinum, osmium, iridium; (II.) sodium, copper, silver, gold; (III.) magnesium, zinc, cadmium, mercury; (IV.) aluminium, thallium, indium, gallium; (V.) silicon, tin, lead.

The data collected were not very concordant, but when they had been compared and the most probable values taken, laying due stress on the purity of the substances examined and the standing of the observer, various regularities or laws were at once apparent, and it is for the purpose of pointing out one of these that the following paper has been written.

This piece of paper, taken as a whole, has certain properties, a certain size, a certain weight, a certain motion, and is the seat of a certain force which attracts other ponderable bodies to it. A single atom of matter has its weight, motion, size, and force. The weights of the atoms form the basis of stoichiometric chemistry, their motion that of the kinetic theory of heat. To their size less attention has been paid; we have only Mendeleeff's curve and certain experiments of Roberts-Austen, who has shown that the tensile strength of gold is weakened, not in proportion to the weight of the metal alloyed with it, but to the volume, in the same way as ten lumps of gravel weaken a casting more than ten grains of sand. Of the force—the force of cohesion—still less is known, in fact absolutely nothing, and the object of this note is to point out what the nature of this force is and what its laws are.

In its early youth science was riotously extravagant of ethers, and any puzzling phenomenon was considered warrant enough for the creation of a new one. As it has grown older it has grown also more economical, until at the present day the scientist who should ask for an appropriation of a new ether, to help him out of a difficulty, would be frowned upon. For this reason, if no other, we will confine ourselves to examining the various means by which our present ether has been supposed capable of producing the forces which cause cohesion.

1. *Gravitation*.—There have not been wanting eminent scientists who have considered that gravitation could account for cohesion, and there have been many ingenious theories proposed, for instance, that of Watts, who supposed that (since the effects of gravity on the moon's path may be supposed to consist of two parts, one independent of the shape of the earth and varying inversely as the

square of the distance, the other dependent on the shape and varying inversely as the cube of the distance), if the atoms were of irregular shapes it might account for the effects. But no theory with gravitation as its basis will hold; first, because the effects are much too small; second, because, as we shall see, the cohesive force is totally independent of the weights of the atoms and depends on the size only.

2. *Condensation and Rarefaction of the Ether caused by the Motion of the Atoms*.—If we hold a pith ball near a tuning fork the pith ball will be attracted up to a certain distance, and will then be repelled if brought closer. This theory has been a favourite with many, but as such an attraction would vary with the motion of the atoms in a way that we know the force of cohesion does not, it also must be dismissed.

3. *Electricity*.—That the force of cohesion was due to electricity has long been vaguely suspected, on the same principle apparently that electricity was considered to be the cause of life, i.e., "Life is a wonderful thing and unexplainable, electricity is a wonderful thing and unexplainable; therefore electricity is life."—the argument being possibly aided by an instinctive recollection of the Athanasian creed, which states that "there is only one incomprehensible." The writer is not aware that any evidence in favour of this theory was ever offered, so it was probably merely a guess.

Having rejected theories 1 and 2, we may see how the facts agree with the theory that cohesion is an electrostatic effect.

If we electrolyse a solution of silver nitrate, we know from Faraday's work that every atom of silver deposited on the electrodes carries over a certain quantity of electricity. This quantity is always the same, no matter how or when or where we perform the electrolysis, and this quantity seems to be related to the atoms in the same way as a pint of water to a pint measure. We may calculate the quantity on each atom in the following way. One c.c. of silver weighs about 10.5 grms. One coulomb is carried over by every 1.12 m.grms. of silver deposited, therefore the charge on the atoms contained in one c.c.

of silver is $\frac{10500}{1.12} = 10^4$ coulombs.

As the sizes of the atoms vary from 10^{-7} to 10^{-8} c.m. in diameter, and silver is a small atom ($\frac{1}{4}$ the size of potassium), we may call its size 10^{-8} c.m. In a c.c. of silver then there would be 10^{24} atoms, which would give as the charge on each atom $10^4 \div 10^{24} = 10^{-20}$ coulomb. The capacity of an atom having a diameter of 10^{-8}

c.m. is $\frac{10^{-8}}{18 \times 10^{11}} = 0.5 \times 10^{-20}$ farads.

The potential on each silver atom will therefore be about one volt. We may look at the c.c. of silver as being made up of planes, each plane consisting of one layer of atoms. The distance between the centres of any two layers would be 10^{-8} c.m. The potential on the atoms being one volt, the attraction between any two layers would be—

$$\frac{4.5 \times 10^{-11} \times 1^2}{10^{-16}}$$

grms. per c.m.² = 4500 kg. per c.m.² = calculated tensile strength of silver = 45 kg. per sq. m.m.

From Wertheim's results we have:—Observed tensile strength of silver = 38 kg. per sq. m.m. That the calculated and observed results should be so close is, of course, only a piece of good fortune. We have no right to expect it, and the data on which the calculation is based is not known with sufficient accuracy. Still, the result is a remarkable one, and places beyond question the fact that the known electric charges on the atoms can produce effects of the same order as those observed.

Having shown this, we may follow up the theory by investigating in what way the cohesion of the metals would vary if this were the case. Evidently (since every atom, large or small, has the same quantity of electricity,

and the larger the atoms of a metal the farther away the centres of the atoms would be) the cohesive force should be inversely proportional to some power of the size (or atomic volume, as it is called, and which is got by dividing the atomic weight by the density of the substance). The following table shows this to be the case. In the first column are the names of the metals; in the second their relative sizes, or atomic volumes; in the third their rigidity, as given by Mr. Sutherland in the *Philosophical Magazine*, August, 1891:—

I.	II.	III.	IV.	V.
Iron	7.1	750 × 10 ⁹	483 × 10 ⁹	550 × 10 ⁹
Copper .. .	7.1	430	483	550
Zinc .. .	9.2	350	314	340
Silver .. .	10.2	280	270	270
Gold .. .	10.2	270	270	270
Aluminium	10.4	250	250	260
Magnesium	14.0	150	154	143
Tin .. .	16.0	136	122	100
Lead .. .	18.0	84	100	83
Cadmium .	13.0	No data.		170 calculated.

As will be seen, the agreement is perfect, with the exception of iron, and those who are aware how greatly the properties of iron are changed with the least particles of impurity will possibly agree with me in thinking that absolutely pure iron would be less rigid; in fact, some recent experiments show that it is so, being nearer 600 than 750; but I have not inserted this value, because a comparison with a set of observations made by one observer at one time and by one method would have a greater value than comparison with a lot of picked results from different observers.

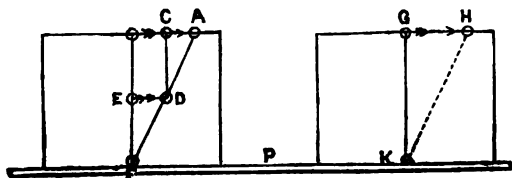


FIG. 1.

FIG. 2.

Assuming the electrostatic theory, we can easily calculate the exact function which rigidity should be of the atomic volume in the following way:—

Suppose Figs. 1 and 2 to represent 2 c.c. of different elements, of which the atoms of one are twice the diameter of the other, or, to put it more accurately, the distance between centres of atoms is twice as great in the one case as in the other. Let 1 contain the smaller atoms. Suppose one face made fast to the plank, *p*, and both sheared slightly till they have the position shown by the dotted lines. It is evident that the ratio of work done in bringing the atom at *g* over to *h*, to that done in bringing *e* to *d*, or *c* to *a*, will be the ratio of the force of attraction between *k* and *g* to that between *e* and *f*. This latter varies inversely as the square of the distance, according to the well-known electrical law; and, consequently, as the distance *gk* is twice that of *ef*, the work done in moving *e* to *d* will be four times that done in moving *g* to *h*. Again, in Fig. 1 there will be 2³ as many atoms to be displaced as in Fig. 2, so that, on the whole, there will be 2³ × 2² as much work done in displacing the cube in Fig. 1 as in Fig. 2. In other words, the rigidity will vary inversely as the fifth power of the distance between the centres of the atoms, or as (atomic volume)^{2/5}. Col. IV. gives the results calculated on this theory. As will be seen, they agree fairly well, as well as could be expected, considering the fact that we have left out one factor. This is the variation of rigidity with temperature, and as it would be obviously unfair to compare lead and silver at 600° C., it is obvious that our calculated results should

only be applied when the metals are at some one point, say, at a temperature which is one-fourth the temperature of their melting-point. As those metals having the greatest atomic volume, as a rule, melt at lowest temperature (though there are many exceptions to this) we may make a rough sort of formula, which shall give the rigidity at ordinary temperatures by multiplying again by the atomic radius, so we get (atomic volume)^{3/5} as the rate at which rigidity varies with size of atoms. Col. V. is calculated in this way from the rough formula—

$$\text{Rigidity} = \frac{28 \times 10^{13}}{(\text{atomic volume})^{2/5}} \quad \dots \text{Equation I.}$$

The formula for Col. IV., and the more correct one, if we neglect variation of rigidity with temperature is—

$$\frac{12560 \times 10^9}{(\text{atomic volume})^{3/5}} \quad \dots \text{Equation II.}$$

The other moduli are related to that of rigidity. For if we represent Young's modulus by $\frac{Y}{a}$, then the modulus of rigidity is represented by—

$$\frac{Y}{2(a+b)}$$

and the bulk modulus by—

$$\frac{Y}{3(a-2b)}$$

where *b* represents the lateral shortening accompanying the longitudinal lengthening *a*. So if *b* bears to *a* any constant ratio, then Young's modulus and the bulk modulus will each be some fraction of the modulus of rigidity. The

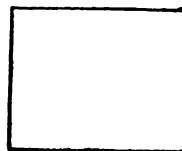


FIG. 3.

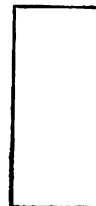


FIG. 4.

Continental writers, at least a good many of them, hold that $\frac{b}{a} = \frac{1}{4}$. Kelvin, Tait, and Stokes say there is no

relation. On the one hand, it is certain that $\frac{b}{a}$ is not constantly equal to $\frac{1}{4}$. On the other hand, it does not follow that there is no relation between the two, and the evidence which has been brought to prove this has no value, for we have no right to argue from the facts that in indiarubber $\frac{b}{a} = \frac{1}{2}$,

while in cork $\frac{b}{a} = \frac{1}{100}$, that $\frac{b}{a}$ does not have any constant ratio in metals. The laws which govern the moduli of compounds and non-homogeneous substances like indiarubber and cork are not the same as those which govern homogeneous substances like gold and silver.

(To be continued).

Determination of Starch and Action of Dilute Acids upon Cellulose.—M. Guichard.—Various procedures which succeed with free starch are of little or no value with cereals. Cellulose, though it has no rotatory action, acquires such a property by saccharification, and has then an effect upon determinations of starch. Its effects are partly annulled by the inverse rotation due to the nitrogenous substances.—*Bull. de la Soc. Chim. de Paris.*

NOTICES OF BOOKS.

Odorographia: A Natural History of Raw Materials and Drugs used in the Perfume Industry. Intended to serve Growers, Manufacturers, and Consumers. By J. CH. SAWER, F.L.S. London: Gurney and Jackson (Successors to Mr. Van Voorst). 1892. 8vo., pp. 384.

THE sense of smell, though of far greater importance in scientific research than that of hearing, has been strangely neglected. It has not been systematically trained, and no attempts of moment have been made to intensify, direct, or record its indications. For the nose we have nothing at all analogous to the "scopes" and the "phones" with which the eye and the ear are respectively armed. Hence we must warmly welcome a treatise like the present, which, though its main purpose is commercial and industrial, must still help to draw attention to the latent capabilities of this sense.

The author in his introduction very correctly says that no sense is capable of receiving such delicate impressions as that of smell, and that none retains them so permanently. The eye, even with the wonderful aid of the spectroscope, is unable to recognise such delicate distinctions, either qualitative or quantitative, as does that of smell. Mr. Sawyer quotes H. H. Fischer and Pentzoldt, of Erlangen, for the experimental result that air containing

1
23000000000 of a mgrm. of mercaptan in a c.c. of air can be recognised. But what of certain insects, e.g., members of the genera *Saturnia*, which can detect the presence of a virgin female of their own species at distances exceeding a mile, even though woods, eminences, houses, &c., intervened? But the delicacy of this sense, even in mankind, is little recognised. It is on record that a little girl, born blind and deaf, and being brought up at an orphan asylum, was employed in sorting the clothes of the children as they came back from being washed. By smell alone she was able to distinguish the socks of the boys from those of the girls!

It must surely make every chemist and biologist crave for the due culture of a sense which, in an unassisted state, can perform such wonders.

The author gives an interesting list of plants which emit powerful, peculiar, and often offensive odours, the cause or the function of which has in many cases not been traced. Here, we cannot help saying, is a field of research open to chemists who have the opportunity of obtaining such plants in a recent condition and in quantity.

The author describes, in successive chapters, organisms which serve as the sources of well-known and admired scents. Foremost come musk and its allies, which are secreted not merely by the musk-deer, the civet, the muskrat, and other mammalian species, but by alligators and certain insects. *Aromia moschata*, a longicorn beetle, formerly common near Tottenham, but now banished by the encroachments of "Jerry, the builder," is said to emit a strong smell of musk at pleasure.

In the next chapter the author discusses the odour of the rose. This well-known perfume cannot be extracted and concentrated in perfection by distillation, but only by maceration in pure grease followed by "enfleurage."

It is an interesting fact that although vaseline and other mineral fats absorb perfumes very readily they do not retain them, and are consequently of no use for the manufacture of pomades and scented oils. One of the largest firms at Grasse informs the author that purified grease and olive oil are the best materials at present known. Here also is a suggestion for research.

The citrine odours—orange flower, neroli, syringa, gardenia, &c.—form another important type. It is said that Curaçao yields the bitterest of bitter oranges and the sweetest of sweet oranges, but that lemons and limes if planted there turn sweet and die. Here are more problems

The fourth chapter takes up the jasmine type. There are upwards of one hundred species of jasmine known, all save one or two natives of the hottest parts of the Eastern hemisphere. To the same class belong the jonquil, the hyacinth, and the tuberose. Why does the author call this plant *tubéreuse*?

The "odour of the hayfields" seems due to kumarine, which we have transmogrified into "coumarine." Its presence has been traced in *Anthoxanthum odoratum*, in a number of other grasses, in ferns, orchids, in the date-palm, and in other plants belonging to very various orders.

Space does not allow us to prolong our examination of this most interesting work. We notice with pleasure that the author promises a second volume. He does not omit to call attention to the scope for flower-farming in our tropical and sub-tropical colonies.

Notes on Qualitative Chemical Analysis. By P. LAKSHMI NARASU NAYUDU, B.A., Professor of Physical Science, S.P.G. College, Trichinopoly. Madras: K. Murugera Chetty, 1892, 8vo., pp. 122.

WE are exceedingly glad to see our Indian fellow-subjects pressing forward in the study of Science; but we cannot help suggesting that they might employ their time and their abilities better than by compiling elementary manuals. However good they may be the language is overstocked with similar treatises. On the other hand, India abounds in products which have not been thoroughly examined, if at all, and presents numbers of phenomena requiring a closer study. We submit, in all courtesy, that the author might preferably turn his attention to such questions.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 14, October 3, 1892.

On Fossil-Wood containing Fluorine.—Dr. T. L. Phipson.—The author examined a specimen of fossil-wood from the Isle of Wight which contained 32.45 per cent of phosphoric acid and 3.90 per cent of fluorine. It seemed to have been fossilised by calcium phosphate and fluor-spar.

Identity of Cascarine with Rhamnoxanthine.—Dr. T. L. Phipson.—The yellow, crystalline substance described by M. Leprince (*Comptes Rendus* of August 1, 1892), as extracted from *Cascara sagrada* is identical with the substance which the author extracted from the bark of *Rhamnus frangula*, to which he ascribes in the CHEM. NEWS the composition $C_{12}H_8O_5$. The two substances are alike in their composition and in their reactions.

A Respiratory Globuline contained in the Blood of the Chitons.—Dr. A. B. Griffiths.—The blood of these creatures is yellow, but the pigment is a luteine or lipochrome, and possesses no respiratory function. The blood contains a colourless respiratory globuline containing no metal in its molecule, but possessing the same properties of oxygenation and de oxygenation as hæmoglobine, hæmocyamine, pinna globine, chlorocruorine, &c. The author ascribes to this compound the formula $C_{621}H_{814}N_{175}SO_{169}$. When charged with oxygen it is colourless.

Influence of the Electric Light on the Structure of Herbaceous Plants.—Gaston Bonnier.—In the author's experiments the electric light has been maintained

without ceasing, night and day, for seven months, and if it was desired to try the effects of discontinuous light the plants in question were covered with black screen. Certain plants perished even under an intermittent light; others manifested an exuberant growth with a more intense verdure of the leaves and a deeper colour of the flowers. The modifications are analogous to those which occur in the plants of high latitudes. The structure of the leaves was in some cases modified so that they could scarcely be recognised. Direct electric light is injurious to the normal developments of the tissues, even at a distance of more than 3 metres, in consequence of the ultra-violet rays.

Zeitschrift für Analytische Chemie.
Vol. xxxi., Part 4.

Apparatus for Obtaining Gases absorbed in Water by a Combination of the Mercurial Pump with Ebullition.—F. Hoppe-Seyler.—This paper requires the accompanying illustration.

Method of Separating Sulpharsenic Acid from Sulphoxyarsenic Acid.—Le Roy W. McCay.—The method is founded on the following facts:—1. If the solution of an alkaline sulpharsenate is distinctly acidified with sulphuric or hydrochloric acid the salt is instantly decomposed, with an escape of hydrogen sulphide and a separation of arsenopentasulphide:—



2. If a highly dilute, strongly refrigerated solution of an alkaline sulphoxyarsenate is slightly acidulated with dilute sulphuric acid, the salt is decomposed and the sulphoxyacid is set at liberty. Under these circumstances it is not decomposed into arsenious acid and free sulphur, but remains quite unaffected. The ice-cold solution remains perfectly clear for hours, and the presence of traces of hydrogen sulphide does not occasion the slightest perceptible decomposition. In order to separate the two acids from each other it is merely necessary to dilute the solution strongly (500 c.c. water to 0.1275 gm. $\text{As}_2\text{O}_5\text{S}_2$), and to refrigerate down to about 0°. On account of a possible gradual decomposition of sulphoxyarsenic acid into arsenious acid and free sulphur, the filtration should be effected as quickly as possible, for which purpose the Bunsen filter-pump is very useful. The following salts were employed:—Bouquet and Cléçz's potassium sulphoxyarsenate ($\text{H}_2\text{KAsO}_4\text{S}$), of a high degree of purity, and a sodium sulpharsenate ($2[\text{Na}_3\text{AsS}_4]15\text{H}_2\text{O}$), which gave on analysis 38.07 instead of 38.08 per cent. As_2S_5 . In the separation I proceeded as follows:—The salts were dissolved in 500 c.c. of water at the temperature of ice, and the solution was then mixed with a slight excess of dilute sulphuric acid. The bottle containing the solution was set in a mixture of ice, common salt, and water, and a violent current of air was drawn through the liquid for about fifteen minutes. After the air has been shut off and the pentasulphide is deposited, the clear supernatant liquid is decanted off, filtered through a Gooch crucible; the precipitate is placed in the crucible and well washed, first with water and then with alcohol. The precipitate is dried at from 105°—110° until the weight is constant, and it is then extracted from six to eight times with carbon disulphide, washed with absolute alcohol, dried again, and weighed. It has been found that this extraction is essential in order to the 0.001–0.002 gm. of sulphur insoluble in cold alcohol and almost invariably mixed with the arsenopentasulphide. The cold, clear filtrate, which scarcely smells of sulphuretted hydrogen, is treated with chlorine, concentrated to a small volume, and placed in a pressure bottle holding about 200 c.c. The bottle is filled up with water which has been recently boiled, the liquid is treated with a strong current of sulphuretted hydrogen until it becomes opalescent, the stopper is firmly inserted, and the whole is heated for an hour in a boiling water-bath.

The pentasulphide is then filtered off, completely washed with water, and then with absolute alcohol, in order to remove traces of sulphur, dried at from 105°—110° until the weight becomes constant and weighed.

On Iodometry.—Theod. Salzer.—This paper will be inserted in full.

Analysis of Horse-Fat.—C. Amthor and Julius Zinc.—The authors give for the kidney fat of horses the following determinations:—

Specific gravity at 15°	0.9320
Melting-point	39°
Congeaing-point	22°
Melting-point of the fatty acids	36°–37°
Congeaing-point	30°–30.5°
Hehner's number	95.47
Reichert's number	0.33
Saponification number	198.7
Acid number (i.e., m.grm. KOH to 1 grm. fat)	1.73
Acetyl number	6.64
Iodine number	81.09
" " the fatty acids	83.88

The consistence of the fat is that of a soft salve, and its colour is a golden yellow.

Determination of Aluminium Phosphate by Precipitation from its Solutions with Ammonia and Alkaline Acetates.—G. Glaser.—This paper will be inserted at length.

On Boyer's Method of Determining Nitrogen.—C. Arnold and Conrad Wedemeyer (see *Comptes Rendus*, cxiii., p. 503).—Already inserted.

An Easy Method of Determining Nitrogen in Nitrates.—C. Arnold and Conrad Wedemeyer.—This paper will be inserted in full.

Action of an Iron Copper Couple upon Nitrates and Nitrites in Sulphuric and Hydrochloric Solutions.—Karl Ulsch.—This memoir is too voluminous for insertion.

Determination of Tartar in Sweet Wines, according to the Method of Berthelot and Fleurien.—Dr. E. Ackermann.—Already inserted.

Attempt at the Detection of Foreign Fats in Butter.—Dr. J. Erdélyi.—The author, after referring to the defects of existing methods, recommends the use of cumol. The clear filtered samples of fat or mixtures of fats are placed for from 24 to 48 hours in an ice-closet. Two c.c. of each are then introduced into dry tubes most carefully cleansed, each of 2c. m. internal diameter; 6 c.c. of cumol are then added to each, and they are allowed to stand at the temperature of a dwelling-room for 24 hours longer. The tubes, along with thermometers, are then surrounded with crushed ice for one hour, and are then lifted out for a moment for examination at certain intervals of time. Their clearness or turbidity in certain times characterise the fats.

Apparatus for the Uniform Mixture of Large Quantities of Pulverulent Substances.—C. Mann.—This paper requires the two accompanying figures.

Self-Acting Filtration Apparatus.—Prof. F. Albin Hoffmann.—This paper cannot be intelligibly reproduced without the illustration.

Detection of Salicylic Acid in Salicylaldehyd and in Salicylic Methyl ester.—A. Schneegans and J. E. Gerock (*Journ. d. Pharm. von Elsass-Lothringen*).—The authors utilise the circumstance that the well-known violet colour which the above compounds produce with ferric salts is permanent on shaking with ether only in case of salicylic acid, whilst in the aldehyd and ester it disappears. Chloroform, amyl alcohol, acetic ethylester, carbon disulphide, petroleum ether, paraffin oil, benzene, toluene, xylene, and pure acetone act similarly to ether. The sensitiveness of the salicylic acid reaction is not impaired by the presence of aldehyd or ester.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 14.

On a Tetramethylmetadiamidic Benzidine.—Ch. Lauth.—This compound, $C_{16}H_{22}N_4$, is a colourless base which crystallises in long needles; it is very soluble in hot benzene and alcohol, from which it is almost entirely deposited on cooling. Boiling water dissolves it very slightly. Its sulphate, hydrochlorate, nitrate, and acetate are very soluble in water. With ferric chloride it gives a colour which is first orange and then brown; with lead peroxide, in presence of acetic acid, a yellowish brown colour; with bichromates a bright orange; with nitric acid a fine violet, changing to a brown.

The Complete Elimination of Barium in Salts of Strontium.—MM. Barthe and Falières.—The authors reply to the criticism of J. Cannepin on their process; the latter seeks to maintain that barium sulphate precipitates strontia from its saline solutions, and takes its place so as to yield a soluble barium salt.

The Calorific Power of Coal and the Formule used for its Determination.—M. Scheurer-Kestner.—The author asserts that there are coals the combustion-heat of which exceed that of their elements, though they are uncommon.

The Analysis of a Ferruginous Sulphated Water named "de Roufauque" found on the Territory of Collioure in the Eastern Pyrenees.—J. Ch. Essner.—A paper of no general interest.

A Study on the Constitution of Milk, its Acidity or Alkalinity.—L. Vaudin.—The milk of mammalian animals has an acid reaction at the moment when it issues from the teat. The value of the acidity of normal milk yielded by females of one and the same species is relatively little variable. All influences which may occasion a disturbance in the secretion (gestation and parturition, regimen, nature of the soil, &c.), occasion a modification in the acidity. The acid reaction of milk is mainly due to the proteic matters present. The variations of acidity which occur in the course of lactation depend on modifications which occur simultaneously in the nature and the relative proportions of the various proteic matters and of the mineral elements of milk.

Alcoholometers of Precision.—J. A. Müller.—The author finds that certain alcoholometers under official control, and guaranteed as exact by dealers, indicate as a mean 0.2 to 0.3 per cent less alcohol than the quantity deduced from the densities.

The Application of Metaphosphoric Acid to the Separation of the Albumenoids of Milk to the Determination of Lactose.—G. Denigès.—This paper does not admit of useful abridgment.

Specific Determination of Xylose.—G. Bertrand.—Already inserted.

Action of Nitric Oxide upon the Metals and the Metallic Oxides.—Paul Sabatier and J. B. Senderens.—Already inserted.

A New Gas-Volumeter.—J. A. Müller.—An intelligible reproduction of this paper is not practicable without the accompanying figure.

Action of Sulphur in Presence of Water upon the Polybasic Acids.—J. B. Senderens.—Already inserted.

Preparation of Methylbenzoylanilide.—J. Dupont.—The author heated in an alcoholic solution equivalent parts of benzoylanilide potassa and methyl anilide. The methyl iodide has certainly been saponified, but the benzoylanilide had remained absolutely unaltered.

Chemical Constitution of Camphor and of Oil of Turpentine, as well as of their Principal Derivatives.—L. Bouveault.—This lengthy paper does not admit of useful abridgment.

Anisoles, Novel Colouring-Matters.—P. Monnet.—Already noticed.

Cryoscopic Studies in the Benzenic Series.—J. Haüsser.—The author has studied the sulphonic acids of benzene from the cryoscopic point of view, and has recognised that these acids have in water molecular depressions different from those of the greater part of other organic substances. The constant 19 of organic substances found by Raoult with very rare exceptions does not exist for these bodies.

Action of Potassium Permanganate upon Organic Acids. Production of New Manganic Salts.—Aug. Lumière and Alph. Seyewetz.—This paper will be inserted in full.

The Chloro-Derivatives of the Isobutylamines.—A. Berg.—The author has studied monochloroisobutylamine, dichloroisobutylamine, and chlorodisobutylamine.

Action of Alcoholic Soda upon Chlorodiamylamine and Chlorodisobutylamine.—A. Berg.—An examination of amylamylidenamine and isobutylisobutylidenamine.

New Process for Obtaining the Cyanamides.—A. Berg.—The author has obtained diamyl- and diisobutylcyanamide by causing potassium cyanide to act upon the chloro-derivatives of diamylamine and diisobutylamine.

Transformation of Gallic Acid into Pyrogallol.—Melting-Point of Pyrogallol.—P. Cazeneuve.—If we add to gallic acid double its weight of aniline, the mixture, which is at first liquid, solidifies abruptly with a rise of temperature. There is formed, doubtless, aniline gallate. If the mass is heated we observe at about 120° a regular development of carbonic acid without appreciable rise of temperature. At this temperature the whole of the gallic acid may be decomposed. On heating to 180° and cooling, aniline pyrogallate is obtained in long crystalline needles very instable. Most of the liquid aromatic amines form an equally favourable medium for the transformation of gallic acid. The melting-point of pyrogallol is 132° (not corrected), and not 115° as asserted in the text-books.

MEETINGS FOR THE WEEK.

FRIDAY, 28th.—Physical. (1) Discussion of Mr. Williams's paper on the "Dimensions of Physical Quantities." (2) Discussion of Mr. Sutherland's paper on the "Laws of Molecular Force," to include papers by Dr. Young and Mr. Thomas on the "Determinations of Critical Density, Critical Volume, and Boiling-Points."

TO CORRESPONDENTS.

R. H. Laverick.—We would suggest inspissation of the juices at a low temperature under reduced atmospheric pressure, or perhaps preferably in a current of hydrogen or nitrogen.

N. P. Martin.—Consult a memoir on "Analysis of Alloys containing Copper, Zinc, and Nickel," by Thomas Bayley (*Phil. Mag.* July, 1878), or, "Brann's Metallic Alloys," 1889.

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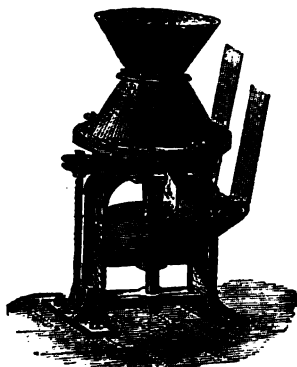
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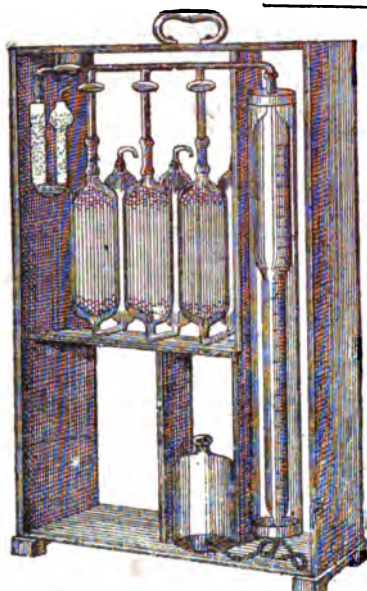
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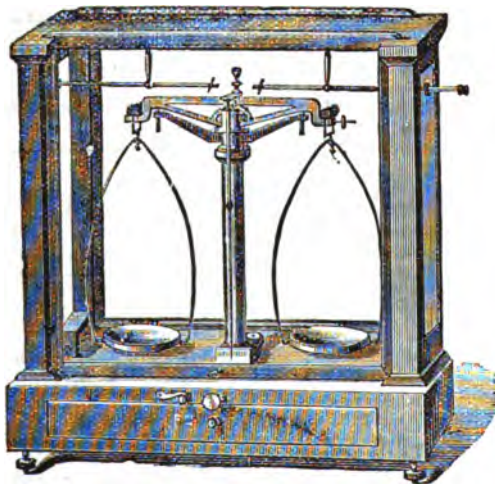


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THE CHEMICAL NEWS.

VOL. LXVI., No. 1718.

ON A VANADIFEROUS LIGNITE FOUND IN THE ARGENTINE REPUBLIC, WITH ANALYSIS OF THE ASH.*

By JOHN J. J. KYLE, Sc.D.,
Professor of Chemistry in the University of Buenos Ayres;
Assayer to the Argentine Mint.

By order of the Minister of the Interior of the Argentine Republic, the Director of the National Board of Works forwarded to the author a small sample of coal taken from a seam recently discovered near the town of San Raphael, in the Province of Mendoza, with instructions to analyse the mineral and to report on its value as a combustible.

The coal is lustrous, black, even when finely pulverised, without fibrous structure, and remarkably brittle. On being heated it softens, emits much gas, which burns with a smoky flame, yielding a light spongy coke, which after combustion leaves a singularly small amount of a greenish coloured ash. The condensed products of its distillation have an acid reaction. The specific gravity of the mineral = 1.173. Its proximate analysis gave:—

Loss on drying at 100° ..	2.05
Volatile matters	49.51
Fixed carbon	47.81
Ash	0.63

100.00

In the elementary analysis, the carbon and hydrogen were determined by combustion with lead chromate; the nitrogen by combustion with soda-lime, and the sulphur by Eshka's method. Its composition, deducting hygroscopic water and use, was found to be as follows:—

Carbon	60.59
Hydrogen	8.63
Nitrogen	1.43
Sulphur	4.23
Oxygen	25.12

100.00

In the calorimetric assay by Berthier's method 1 grm. was found to reduce 23.102 grms. of lead = 5405 heat units. Judging from the above analyses the mineral would appear to resemble most of the bituminous lignites or tertiary coals which occur in this Republic and in Chile. These, however, generally contain a high percentage of ash, the sulphur being chiefly present as iron pyrites. It is evident that such is not the case in the San Raphael mineral, as the percentage of ash is very low, and as will be seen from the analysis later on, this only contains a small proportion of iron oxide. The sulphur determination was carefully repeated with every possible precaution to avoid error, such as might occur from impurity in the reagents, the crucible being heated by an alcohol flame. It would therefore appear that the sulphur must for the most part be present either in the free state or in some form of combination with the organic elements.

The remarkably small percentage of ash and its peculiar greenish colour naturally attracted my attention. On treating it with hydrochloric acid there appeared a deep red colouration, which, on dilution and heating, changed to a greenish blue. On addition of ammonia in

excess the colour disappeared, showing it had not been due to traces of copper, as I had at the first supposed. On further investigation I satisfied myself that the ash contained *vanadium*, and was induced to continue its study as thoroughly as might be possible, considering the small quantity (about 500 grms.) of raw material at my disposal. The mineral was incinerated in a platinum dish over a Bunsen flame, and the ash, still retaining some carbon, was reserved for analysis. The qualitative analysis showed it to contain:—

Soluble in water—

Ca, K, Na, V₂O₆, SO₃, and Cl (trace).

Soluble in HCl—

Fe, Al, Ca, Mg, V₂O₅, Pb₂O₅, SO₃ and Mn (trace).

Insoluble in HCl—

SiO₂, Al, Fe, Mg, Ca (trace), and carbon.

In the course of the qualitative examination I had abundant proof that the ash contains a large proportion of vanadium, so that the quantitative methods required to be carefully chosen, to avoid waste of the very limited supply of material, and at the same time secure completeness and accuracy in the results.

The following plan was adopted, in the description of which I shall omit unnecessary details. I have been much indebted to a paper by Dr. Adolfo Doering on the "Separation and Quantitative Estimation of Vanadic Acid," published in the *Boletín de la Academia Nacional de Ciencias en Córdoba, Rep. Arg.* (vol. v., p. 117), and have taken advantage of the author's suggestions with regard to the separation of vanadic acid from iron and alumina and its precipitation as mercurous vanadate.

One grm. of the ash was repeatedly digested in hot dilute nitric acid; the insoluble silicates and carbon were washed on a tared filter, dried at 120°, weighed, ignited to remove carbon, and the weighed silicates reserved for further investigation.

The nitric solution, after removal of excess of acid, was nearly neutralised by sodium carbonate, acetate of sodium added, and, on boiling, iron and aluminium phosphates and vanadates were thrown down. The precipitate was dissolved in nitric acid, some sodium phosphate was added, and the phosphates again precipitated by sodium acetate, the vanadium being retained in solution. The mixed phosphates were collected and weighed, the iron contained in these converted into sulphide, and weighed as peroxide. The phosphoric acid was estimated and its amount *plus* that of the iron oxide deducted from, the weight of the total phosphates, the difference being regarded as alumina. As the determination of the Pb₂O₅ included part derived from the added sodium phosphate, that corresponding to the ash was separately determined. The filtrate containing vanadium and excess of sodium phosphate was precipitated by ammoniacal magnesium nitrate, and as the precipitate retained some V₂O₅ it was re-dissolved, and the treatment repeated until the magnesium and ammonium phosphate was colourless, the mixed filtrates containing the V₂O₅ were acidified with acetic acid, and the V₂O₅ precipitated by mercurous nitrate. The mercurous vanadate was washed with hot water, collected, and carefully ignited to expel mercury, the residue = 0.034 grm. V₂O₅.

The filtrate from the mixed precipitates of phosphates and vanadates, thrown down by sodium acetate as previously mentioned, was nearly neutralised by sodium carbonate, and the V₂O₅ precipitated in the hot liquid by mercurous nitrate; the mercurous vanadate on ignition weighed 0.250 grm. On fusion with sodium carbonate and digestion of the melt with hot water, there remained a residue which weighed 0.008 grm., which being deducted = 0.242 grm. V₂O₅, not combined with iron and alumina. After getting rid of excess of mercury by H₂S, the filtrate, on being neutralised with ammonia assumed a dark colour, and after repose there was formed a very slight precipitate which contained traces of vanadium and manganese sulphides, which were not estimated; the filtrate from

* Read before the British Association, Edinburgh Meeting, 1892.

these was treated by ammonium oxalate, and the lime estimated as usual; traces of magnesia were found in the filtrate but not estimated.

It being now apparent that only a small fraction of the vanadium was in combination with iron or alumina, I treated a fresh portion of ash by digestion in warm ammonia solution, so long as anything appeared to dissolve. The alkaline solution was evaporated in a tared capsule, the residue consisting of calcium sulphate, ammonium vanadate, and vanadates of the alkaline metals. By drying and weighing the residue insoluble in ammonia, which was collected on a tared filter, the amount soluble in ammonia was ascertained. The filter was then ignited and the residue weighed, thus controlling the previous carbon determination. The residue was digested in hot nitric acid and the solution employed to determine the phosphoric acid by means of molybdate of ammonium.

The mixed vanadates and calcium sulphate left on evaporation of the ammoniacal extract were treated with hot water, much of the calcium sulphate remaining undissolved; the V_2O_5 was precipitated by lead acetate, the precipitate collected on a tared filter and washed with hot water, a few drops of ammonium acetate being added to insure removal of any lead sulphate; the lead vanadate was dried at 100° and treated as recommended by Roscoe (Roscoe and Schorlemmer, "Treatise on Chemistry," Vol. ii., Part II., p. 299). As in this method the V_2O_5 is estimated by difference between the weight of the dried lead vanadate and the contained lead weighed as sulphate, the estimation was checked by titration with permanganate of the sulphuric solution, the V_2O_5 having been reduced to V_2O_4 by sulphurous acid. After removal of the excess of lead in the filtrate from the lead vanadate, and of the lime by ammonium oxalate, the filtrate was evaporated to dryness, ignited to expel ammonia salts, the residue moistened with sulphuric acid, again ignited, and the sulphates weighed. The residue dissolved completely in water, the contained SO_3 was on estimation found to correspond to the sulphates regarded as potassium sulphate; the sodium revealed by the spectroscope was therefore a mere trace. As the ash contained no carbonate the lime was calculated as sulphate.

The insoluble silicates were fused with alkaline carbonates, and the melt, being practically free from vanadium, was treated as usual for the estimation of silica and bases.

The composition of the ash after deduction of the carbon (which two separate determinations had shown to amount to 27.8 per cent in the ash as analysed) may be stated as follows:—

Soluble in acid.	Vanadium pentoxide	38.22
	Phosphorus pentoxide	0.71
	Sulphuric anhydride	12.06
	Calcium oxide	8.44
	Ferric oxide	4.98
	Aluminium oxide	3.32
Insoluble in acid.	Potassium oxide	1.73
	Silicic anhydride	13.70
	Ferric oxide	9.42
	Aluminium oxide	5.26
Undetermined traces of	Magnesium oxide	0.83
	manganese, magnesia, chlorine, and loss in analysis	1.33
		100.00

As the analysis of the extract obtained by digesting the ash in hot ammonia water showed that, of the total V_2O_5 , viz., 38.22 per cent, no less than 30.6, say 80 per cent, exists either as a vanadium oxide or as a soluble alkaline vanadate, only the remaining 20 per cent can exist in combination with iron and alumina. I have examined the ash under the microscope, and find it made up of particles having by reflected light the colour of unburnished gold; others are translucent and of a greenish white colour; a few are dark red, and have a metallic

lustre. When heated on platinum foil to the highest temperature of the blowpipe flame, the ash undergoes partial fusion, and acquires a dark red colour and metallic lustre.

On being boiled with distilled water, a yellow solution is obtained, the yellow colour being probably due to the change of the potassium metavanadate into tetravanadate, by far the larger part of the vanadium compounds remaining insoluble in pure water, although, as previously mentioned, readily soluble in hot solution of ammonia.

There appears to be no doubt that the ash contains the vanadium, chiefly as vanadic pentoxide, in a free state, partly as potassium vanadate and also some as iron or aluminium vanadates.

From the foregoing it is evident that the San Raphael coal is one of great interest, being not only of fair quality as a combustible, but being also available as a source of vanadic acid for industrial purposes, seeing that each ton of the mineral, supposing it to be equal to the sample, will produce over 14 lbs. of pure ash containing $4\frac{1}{2}$ lbs. of the vanadic pentoxide, of which $3\frac{1}{2}$ lbs. may be extracted by simple treatment of the ash with an alkaline liquor, whilst the remainder is of course susceptible of extraction from the insoluble part as in the case of the basic slags of Creusot (*Compt. Rend.*, xcv., 42–44), which contain but 1.5 per cent.

In short, the ash of the San Raphael lignite is, so far as my knowledge goes, the richest known material utilisable as a source of vanadium compounds. I have taken steps to obtain information regarding the carboniferous strata whence any sample of mineral was derived; the details cannot fail to be of great interest. Meanwhile I have been assured that the seam where explored is about one metre in thickness.

The Argentine provinces of Cordoba and San Luis are already well known as sources of vanadium minerals, such as vanadite, Descloisite, and psittacinite; the province of Mendoza must now be added to the list of localities in the Argentine Republic where is to be found vanadium.

NEW METHODS FOR QUANTITATIVE ANALYSIS.*

By A. BAUMANN.

(Continued from p. 206).

Determination of Barium.

THE determination of barium in the manner given for lead and bismuth presents certain difficulties, as on precipitating a neutral solution of barium chloride with potassium bichromate, hydrochloric acid is set free and holds barium chromate in solution. If the precipitation is effected with neutral potassium chromate, the barium precipitate always carries down along with it some potassium chromate, which can not be removed by washing without much difficulty. On the contrary, ammonium chromate appears very suitable. It was first proposed by P. Schweitzer for the precipitation of barium, and has since been recommended by R. Fresenius.

For effecting the direct determination the solution of barium is heated to ebullition in a beaker, and a solution of neutral ammonium chromate is then added until the supernatant liquid has a distinct yellow colour. The precipitated barium chromate is filtered off, the portions adhering to the glass and the precipitate itself are washed with dilute ammonium chromate, and a strongly dilute solution of ammonia is ultimately used for washing out the barium chromate. The portions adhering to the beaker are dissolved in a little dilute hydrochloric acid, and the precipitate itself is rinsed with strongly diluted hydrochloric acid (1 : 20), heated to about 60° , into the external space of the gas-generator. In this manner, the

* *Zeit. für Angew. Chemie und Zeit. für Analytische Chemie.*

total quantity of the barium chromate is generally dissolved. Ten c.c. of sulphuric acid are then put in the outer space of the developing-vessel, and the free chromic acid is then determined with hydrogen peroxide in the ordinary manner.

The composition of barium chromate is analogous to that of lead chromate. Consequently four atoms of oxygen evolved correspond to 1 mol. baryta, or 4×15.96 parts by weight of oxygen represent 152.82 parts by weight of BaO ($\text{Ba} = 136.86$). Hence it is calculated that 1 c.c. of oxygen at 0° and 760 m.m. barometric pressure indicates 3.42 m.grms. baryta.

The indirect method which leads more quickly to a conclusion is effected in a quite similar manner. We precipitate in a 100 c.c. measuring flask with an accurately measured quantity of a neutral solution of ammonium chromate, the standard of which has been determined by gas-volumetry, fill up to the mark when cold, filter, and determine the chromic acid which has remained in solution in an aliquot part of the filter.

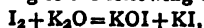
The authors have obtained very satisfactory results in this manner.

Baumann has founded other methods for quantitative analysis upon the behaviour of hydrogen peroxide with iodine. It is already known that oxygen is evolved on the contact of hydrogen peroxide and iodine in an aqueous and acid solution. This reaction does not ensue according to the equation $\text{I}_2 + \text{H}_2\text{O}_2 = \text{O}_2 + 2\text{HI}$; but a simple experiment shows that iodine in water, like manganese dioxide in water and potassium bichromate in a neutral solution, is capable of decomposing a large quantity of hydrogen peroxide without itself undergoing any essential change. Hence this reaction cannot be utilised for the determination of iodine.

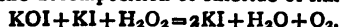
Iodine in an alkaline solution behaves quite differently with hydrogen peroxide. If we dissolve iodine in a cold, saturated lye of potassa or soda there is formed, according to the general assumption, alkali iodate. According to C. F. Schönbein and Berthelot there is formed in analogy to the action of chlorine and bromine alkali hypoiodite.

If upon a solution of iodine in potassa-lye we pour hydrogen peroxide shortly after the reaction of the two substances has commenced, there sets in brisk effervescence in consequence of the escape of oxygen, and the liquid, previously yellow, becomes suddenly colourless. Hence it appears that there was present in the solution not potassium iodate, but a hypoiodite, which like the hypochlorites evolves oxygen.

Iodine, therefore, quite like chlorine, reacts with potassa-lye according to the following equation—



and the decomposition of the compounds formed takes place like the decomposition of chloride of lime—



According to theory, therefore, 2 atoms of oxygen are liberated to 2 atoms of iodine in a watery as well as in an alkaline solution.

In quantitative experiments, however, there is always rather less oxygen evolved than theory requires according to the above equations. This deviation is explained by the instability of potassium hypoiodite. When working with the azotometer the gas-generating apparatus must always be placed in water of the temperature of the room before the commencement of the analysis, so that the rise of temperature which occurs during charging and closing the apparatus may be again equalised. During this short time a part of the potassium hypoiodite passes into potassium iodate and thus escapes determination.

In order to abridge as far as possible the time of the action of the potassa-lye upon the iodine, Baumann brought strongly alkaline hydrogen peroxide in contact with neutral solution of iodine. In these experiments there were obtained to 126.54 parts of iodine exactly 15.96 parts of free oxygen, or exactly the quantity which

the above equations require. Baumann takes this reaction as the basis of the following methods.

Determination of the Free Iodine.

We place in the wider space of the gas-generating apparatus the solution of iodine in potassium iodide, the volume of which must amount to from 40—50 c.c. We allow at first 5 c.c. of hydrogen peroxide (containing about 2 per cent H_2O_2) to flow into the inclined glass cylinder, and afterwards 10 c.c. of a solution of potassa hydrate (prepared by dissolving 1 part of potassium hydroxide in 2 parts of water). A sufficient inter-mixture of the decomposition liquid is effected spontaneously as the heavy solution of potassa is poured upon the hydrogen peroxide.

After the generating-vessel is closed, and the elevation of temperature has been effected in the known manner, water is allowed to flow down from the measuring-tube, and the liquid in the generating-vessel is set in rotatory motion, with the precaution that none of the decomposition liquid is spilt out of the cylinder.

When the solution of iodine is in rapid motion we suddenly mix the two liquids without interrupting the rotatory movement, and shake vigorously as long as an increase of gas is perceptible in the burette. The chief volume of the oxygen is evolved forthwith in the first seconds, and the decomposition is quite complete if we continue shaking for a minute.

If whilst shaking we avoid touching the sides of the vessel with the hand (which is easily effected), the volume of gas may be read off at the expiry of five minutes, since the reaction takes place with a quite unimportant change of temperature. It is not advisable to wait longer than from thirty to forty minutes, since during this time not only the temperature of the water in the cooling vessels may vary, but frequently a slight escape of oxygen may become perceptible, occasioned by a gradual decomposition of the hydrogen peroxide in the alkaline solution. If we omit to set the solution of iodine in brisk circular movement before decomposition, we must expect to find a loss of oxygen of 0.8 c.c. or 1 m.grm., even though the results are sometimes accurate on mixing slowly and using very dilute solutions of iodine. A loss is also frequently experienced if the iodine is dissolved in a smaller quantity of liquid than the instructions demand. If we use the potassa-lye much more dilute than it is indicated above we obtain too high results, as the hydrogen peroxide sets up a decomposition of the iodides formed, with development of oxygen.

The volumes of gas read off are reduced to 0° and 760 m.m. atmospheric pressure, and the product is multiplied by 11.33. Thus we obtain the weight of the iodine in m.grms., as 1 c.c. oxygen at 0° and 760 m.m. atmospheric pressure corresponds to 11.33 m.grm. iodine ($\text{I} = 126.54$). Perfectly accurate results are obtained by following the simple directions given.

This method may be advantageously utilised for standardising solutions of iodine, since, according to Baumann's experiments, iodine can be determined gas-volumetrically with as much accuracy as by titration with sodium thiosulphate and starch-paste. The gas-volumetric method can be completed in a shorter time and does not require the use of the balance.

In order to determine the standard of a solution of iodine, which approximates to a decinormal, we place 40 or 50 c.c. accurately measured in the external space of the gas-developing apparatus, pour the decomposing liquid into the small glass cylinder, and after the temperature has become equalised, shake with the precautions given above. Of more dilute solutions of iodine we use from 60 to 80 c.c.

(To be continued.)

The Chemical Society.—In consequence of the alterations in the rooms of the Chemical Society, the first Ordinary Meeting of the Society will not be held until Thursday, November 17, at 8 p.m.

ON THE REACTIONS OF FERRIC SALTS
WITH SULPHOCYANATES.

By H. M. VERNON, B.A.

(Concluded from p. 203).

The Effect of Temperature on Ferric Sulphocyanate Solutions.

THE effect of the increase of temperature on the various solutions of ferric sulphocyanate was then determined. The method of procedure was the same as that described by the writer in the paper before alluded to; colour determinations being made at 60°, 50°, 40°, 30°, and 20°. The colour effect at 20° was always taken as 100, and the values at other temperatures compared against this. The colour effects of the solutions were always taken at 20°, both before and after heating. The values were the same to within two per cent, so no chemical change was caused in the solution by the heating.

The effect of temperature on the colour of solutions of the various sulphocyanates with 100 equivalents of ferric chloride was first determined. The solutions examined were at dilutions of 160 litres. From the table it will be seen that the colour increase on rise of temperature is about the same for all sulphocyanates. The experimental error in these determinations is considered at about 3 per cent, and none of the numbers differ by more than this amount from the mean values at each temperature.

A similar series of determinations was made with ferric chloride replaced by ferric sulphate. Here the colour effect, instead of increasing on rise of temperature, decreases considerably. This contrary effect is evidently due to the reaction of the acid sulphates formed in the solution, the quantities of which change on variation of temperature. Thus, Ostwald found ("Lehrbuch," ii., 785) that the affinity of sulphuric acid for soda, compared with that of nitric or hydrochloric acid, decreased from 100 at 20° to 82.7 at 60°. The mean value of the colour effects of the various sulphocyanate solutions at 60° is 81.2, but the similarity of these numbers is probably only accidental. The colour effects of the various solutions show greater variations among themselves than those with ferric chloride, the differences being too great to be due merely to experimental error. We should, in fact, expect them to vary slightly with the different sulphocyanates used, as Ostwald has shown that the relative affinity of sulphuric acid to that of nitric or hydrochloric acids varies with the nature of the base.

The colour of a solution of potassium sulphocyanate and ferric nitrate is affected by temperature to the same extent as solutions of ferric chloride and sulphocyanates. The solution of ferric tartrate and lithium sulphocyanate

decreases in colour effect to a much greater extent on heating than ferric sulphate solutions, and even slightly more than a solution of ferric citrate and potassium sulphocyanate. If the lithium salt had been replaced by the potassium salt, the colour decrease would have been about the same as for the citrate. It was not possible to determine the effect of temperature on a solution of ferric acetate and sulphocyanate, as on heating it decomposed, with precipitation of ferric oxide. We see therefore that sulphocyanate solutions reacting with ferric chloride and nitrate, salts of monobasic acids, show considerable increase of colour on heating, whilst with solutions of ferric sulphate, tartrate, and citrate—salts of polybasic acids—show considerable decrease of colour effect on heating.

As the solutions of ferric sulphocyanate become more dilute, or when less ferric salt is present—that is to say, when the ferric sulphocyanate is present in a more unstable state—the tendency is for the colour effect to decrease on rise of temperature. Thus a solution of potassium sulphocyanate and 100 equivalents of ferric chloride at 800 litres dilution shows only half as much increase in colour effect on heating to 60° as the same solution at 160 litres dilution. A similar solution, with the ferric chloride replaced by the sulphate, shows more than twice as great a decrease of colour on heating as the solution at 160 litres dilution. A solution of calcium sulphocyanate and ferric sulphate at 800 litres, though affected considerably more than at 160 litres, is nevertheless not so much influenced as the potassium sulphocyanate and ferric sulphate solution. The solution containing equal equivalents of ferric chloride and potassium sulphocyanate decreases considerably in colour on heating, whilst a similar solution with ferric sulphate is affected to a still greater extent. The colour effect of this solution could not be determined at 50° and 60°, as it began to decompose and became milky; at 45° the colour effect was 40.6.

On heating a solution of a sulphocyanate and the ferric salt of a monobasic acid, as ferric chloride, there must be two influences at work: one causing the colour effect to increase on heating; the other, to decrease. The increase of colour is probably due to the formation in the hot solutions of anhydrous molecules of ferric sulphocyanate, with increase of colour effect. The decrease of colour is probably due to the water having a greater decomposing effect on the unstable ferric sulphocyanate molecules, owing to its greater activity and molecular motion in hot solutions. As has been shown, in the more dilute solutions, or in solutions containing less excess of ferric salt, the decrease of colour influence counteracts and at last overpowers the increase of colour influence. In solutions of ferric salts of polybasic acids there is still another influence at work, namely, the decrease of colour on heating due to the formation of the acid sulphate, tartrate, or

Reacting salts.	Equivalents of ferric salt to 1 equivalent sulphocyanate.	Dilution in litres.	Colour effect at			
			30°.	40°.	50°.	60°.
KSCN.Fe ₂ Cl ₆	100	160	107.8	116.3	127.5	141.0
NH ₄ SCN.Fe ₂ Cl ₆	100	160	107.7	118.3	131.8	144.0
NaSCN.Fe ₂ Cl ₆	100	160	106.8	113.8	132.4	146.3
LiSCN.Fe ₂ Cl ₆	100	160	105.2	114.8	124.8	138.2
Ca(SCN) ₂ .Fe ₂ Cl ₆	100	160	104.1	115.6	124.4	141.3
Ba(SCN) ₂ .Fe ₂ Cl ₆	100	160	107.0	118.0	127.8	141.4
KSCN.Fe ₂ (SO ₄) ₃	100	160	95.7	90.8	88.2	85.4
NH ₄ SCN.Fe ₂ (SO ₄) ₃	100	160	95.2	92.3	89.6	85.1
NaSCN.Fe ₂ (SO ₄) ₃	100	160	92.9	87.8	84.2	78.2
LiSCN.Fe ₂ (SO ₄) ₃	100	160	93.5	87.0	80.5	75.0
Ca(SCN) ₂ .Fe ₂ (SO ₄) ₃	100	160	95.0	89.0	84.6	80.4
KSCN.Fe ₂ (NO ₃) ₆	100	160	107.6	119.2	128.2	139.8
LiSCN.Fe ₂ (C ₄ H ₇ O ₆) ₃	100	160	83.0	69.2	57.7	48.2
KSCN.Fe ₂ (C ₆ H ₅ O ₇) ₂	100	160	88.0	75.1	63.8	50.5
KSCN.Fe ₂ Cl ₆	100	800	105.4	110.1	112.5	117.9
KSCN.Fe ₂ (SO ₄) ₃	100	800	78.2	65.1	55.5	47.9
Ca(SCN) ₂ .Fe ₂ (SO ₄) ₃	100	800	85.6	74.2	67.1	61.1
KSCN.Fe ₂ Cl ₆	1	80	80.2	68.1	52.6	46.8
KSCN.Fe ₂ (SO ₄) ₃	1	80	78.4	55.8	—	—

citrate, as the case may be. Even in concentrated solutions these two decreasing colour effect influences overpower the influence tending to increase the colour effect.

The Effect of Free Acid on Ferric Sulphocyanate.

When a solution of ferric nitrate was prepared, a small quantity of free nitric acid had to be added to bring up the proportion present in the solution to the amount required by the formula $\text{Fe}_2(\text{NO}_3)_6$. It was thought interesting to determine the effect of the further addition of free nitric acid on the colour of a solution of ferric nitrate and potassium sulphocyanate. The results obtained were as follow:—

Equivalents of HNO_3 added.	1:1 Solution, 40 litres dilution.	1:1 Solution, 160 litres dilution.	1:100 Solution, 160 litres dilution.
0	100	100	100
0.1	109.1	134.5	103.6
0.2	116.2	161.4	104.8
0.5	117.4	207.5	105.7
1	117.2	228.4	106.0
2	111.4	228.7	106.0
3	109.8	222.2	—
5	103.9	206.2	—
10	102.2	176.9	—
20	98.1	152.6	—
30	96.0	146.0	—

The numbers in the first column represent the number of equivalents of acid added, compared with the number already present in the solution. Thus to the solution containing 100 equivalents of ferric nitrate, a hundred times as many equivalents of acid would be added as to an equal equivalent solution. The effect of dilution caused by the water added with the nitric acid was, of course, allowed for. As with the heating of a ferric sulphocyanate solution, the effect of the addition of nitric acid is twofold: on the one hand, it causes an increase of colour effect by causing the ferric sulphocyanate to exist in a more stable or less dissociated state; on the other hand, it also dissolves or decomposes some of the salt. On addition of free acid to a certain degree, therefore, the colour effect increases, but after this point, when more acid is added, more ferric sulphocyanate is dissolved than is caused to be re-formed by combination of its dissociated ions, and the colour effect decreases. The great effect the free acid has on the stability of the salts is well shown in the case of an equal equivalent solution at 160 litres dilution, where the addition of one equivalent of acid more than doubles the colour effect. The 100 equivalent solution is but slightly affected by the free acid, which forms an additional proof of the greater trustworthiness of the colour constants for such solutions over those obtained with equal equivalent solutions.

Summary.

The chief conclusions arrived at in this paper are the following:—

Solutions of ferric sulphocyanate are greatly influenced by dilution, owing to the salt undergoing dissociation. Solutions containing great excess of ferric salt or sulphocyanate are most stable; that containing equal equivalents of the salts, the least. On dilution of such a solution from 40 litres to 640 litres, the colour effect is decreased 94 per cent.

The amount of ferric sulphocyanate existing in solutions containing excess of ferric salt decreases on dilution according to the law of mass, but this is not the case with solutions containing excess of sulphocyanate.

On determining the colour reactions of ferric chloride, nitrate, sulphate, tartrate, citrate, and acetate solutions with those of the sulphocyanates of potassium, ammonium, sodium, lithium, calcium, and barium, it was found that the amount of ferric sulphocyanate formed was proportional to the product of two constants: one depending on the nature of the acid of the ferric salt; the other, on

the nature of the base of the sulphocyanate. The colour constants for the acids show considerable resemblance to their relative affinities, but for the bases there is no resemblance.

Solutions of sulphocyanates and the ferric salts of monobasic acids increase considerably in colour on heating, whilst with the ferric salts of polybasic acids the colour effect decreases considerably on heating.

THE CONDITIONS OF THE FORMATION AND DECOMPOSITION OF NITROUS ACID.*

By V. H. VELEY, M.A.

(Continued from p. 201).

If Clemente Montemartini's equation $dc/dT = kC$ is correct, there should be two reacting substances, one of constant concentration throughout the reaction. It is, however, to be observed that the values given for the constant k in his results differ widely among themselves, often as much as 25 per cent between the maximum and minimum. Further, all the results in each set of experiments are referred to the first, the C_0 of equation (ii.), though there is no especial reason that this analytical determination should be more exact than those subsequent to it. With the general purport, however, of Martini's paper I cannot but completely agree, namely, that the rate of decomposition of nitrous acid is dependent upon the tension of the superincumbent nitric oxide, without, however, necessarily committing oneself to the view that herein is presented a "true case of dissociation."

It is worthy of remark that the curve representing the decomposition of nitrous acid is exactly identical with that of a previous case of chemical change investigated by myself, namely, the decomposition of formic acid into carbonic oxide and water (*Phil. Trans.*, 1888, A, p. 290), in which the method of observation was precisely the reverse of that adopted in this research. For, herein, the concentration is determined at equal intervals of time,

SERIES XXIV.

Volume of solution = 70 c.c. Temperature, 25.5°. Ratio of nitrous to nitric acid = 1:2.13.

T.	C (observed). Grm.	C (calculated). $t=400$. Log $k=1.250$.
		Grm.
0	0.4382	0.4448
30	0.4009	0.4147
60	0.3915	0.3877
90	0.3673	0.3640
120	0.3460	0.3430
150	0.3231	0.3244
180	0.2979	0.3075
210	0.2966	0.2924
240	0.2836	0.2851
270	0.2714	0.2661

SERIES XXV.

Volume of solution = 60 c.c. Temperature, 25.0°.

T.	C (observed). Grm.	C (calculated). $t=170$. Log $k=0.856$.
		Grm.
0	0.4157	0.4237
30	0.3646	0.3606
60	0.3190	0.3134
90	0.2881	0.2774
120	0.2484	0.2489
150	0.2381	0.2250
180	0.2102	0.2209
210	0.1894	0.1901
240	0.1647	0.1679

* A Paper read before the Royal Society, June 2, 1892.

SERIES XXVI.

Volume of solution = 70 c.c. Temperature, $24.6^{\circ} \pm 0.1$.
Ratio of nitrous to nitric acid = 1 : 20.7.

T.	C (observed). Grm.	C (calculated), $t = 480$. Log $k = 1.452$.	
		Grm.	
0	0.6707	0.6742	
30	0.6262	0.6270	
60	0.5789	0.5899	
90	0.5537	0.5547	
120	0.5255	0.5255	
150	0.5065	0.4968	
180	0.4775	0.4719	

but in the previous case observations were made of the times required for equal diminution of concentration. The results of other series of experiments are given below, the observed and calculated values for the concentration of the nitrous acid being compared in each instance.

In all the above series of experiments the observed and calculated results are as nearly approximate as can be expected, considering the great instability of the nitrous acid, which is appreciably decomposing even in the brief interval of time required for the transference of the solution from the decomposition flask into the potassium permanganate. In the last series of experiments quoted above, in which a considerable proportion of nitric acid was purposely introduced, it is to be noticed that the rate of decomposition is decreased, even though the mass of nitrous acid originally present was greater, which should of course produce an exactly opposite result. This would, therefore, seem to indicate that nitrous acid is more stable in the presence of excess of nitric acid.

Nitrous Acid from Nitric Oxide and Nitric Acid.

Nitric oxide gas was passed into concentrated nitric acid until a deep green liquid was obtained; 10 c.c. of this were then slowly introduced into about five times its bulk of water, and the whole volume finally made up to 100 c.c.

SERIES XXVII.

Volume of solution = 100 c.c. Temperature, $27.7^{\circ} \pm 0.1$.
Ratio of nitrous to nitric acid = 1 : 10.1.

T.	C (observed). Grm.	C (calculated), $t = 360$.	
		Grm.	
0	0.8812	0.8910	
30	0.8372	0.8227	
60	0.7749	0.7637	
90	0.7021	0.6967	
120	0.6791	0.6684	
150	0.6443	0.6290	
180	0.5874	0.5805	
210	0.5603	0.5627	
240	0.5242	0.5347	
270	0.4965	0.5093	

The curve representing the course of decomposition of the nitrous acid obtained by this method is precisely identical with that of the nitrous acid from the silver nitrite, though the rate of decomposition is somewhat diminished. For if the series above be compared with Series XXV., which lasted for the same duration of time, yet though the mass undergoing change was nearly twice as great and the temperature 2° higher, both of which conditions would increase the rate, yet there is a difference of only 5 per cent in the amount of nitrous acid which has disappeared in the two cases. This result confirms that of the immediately preceding series in showing the increase of the stability of nitrous acid in the presence of nitric acid.

Another set of experiments was conducted, the condition of temperature being varied.

SERIES XXVIII.

Volume of solution = 100 c.c. Temperature, 11.1° to 11.3° .
Ratio of nitrous to nitric acid = 1 : 10.72.

T.	C (observed). Grm.	C (calculated), $t = 860$. Log $k = 1.5811$.	
		Grm.	
0	0.8910	0.8823	
30	0.8716	0.8545	
60	0.8467	0.8266	
90	0.8046	0.8006	
120	0.7815	0.7761	
150	0.7595	0.7531	
180	0.7337	0.7314	
210	0.7033	0.7108	
240	0.6759	0.6914	
270	0.6710	0.6739	
300	0.6454	0.6537	

A third set of experiments was also conducted at a higher temperature, other conditions remaining the same.

SERIES XXIX.

Volume of solution = 100 c.c. Temperature, 31.2° .
Ratio of nitrous to nitric acid = 1 : 10.13.

T.	C (observed). Grm.	C (calculated), $t = 330$. Log $k = 1.3268$.	
		Grm.	
0	0.6565	0.6432	
30	0.6030	0.5893	
60	0.5542	0.5443	
90	0.4939	0.4712	
150	0.4451	0.4422	
180	0.4169	0.4162	
210	0.3970	0.3930	
240	0.3545	0.3720	
270	0.3344	0.3538	

On a comparison of the results set forth in the three preceding series of experiments, it appears that the velocity of decomposition of nitrous acid is an exponential function of the temperature, the former increasing in geometrical as the latter increases in arithmetical proportion. This relation may be expressed by the equation—

$$v_t = v_1 k^{(t - t_1)},$$

that is to say, the difference of the logarithms of the amounts of nitrous acid decomposed at the end of a given interval of time will be constant for a constant difference of temperature. This is rendered evident by the following comparison:—

Series.	Temperature.	Percentage loss after 270° .	Logarithms.
(I.)	11.2°	24.00	1.3802
(II.)	27.7	43.01	1.6334
(III.)	31.2	49.09	1.6909

The logarithmic differences for 1° are therefore:—

From (I.) and (III.)	0.0153
" (I.) " (II.)	0.0154
" (II.) " (III.)	0.0167
Mean	0.0158

The rate of chemical decomposition of the nitrous acid is therefore practically doubled for every 20° , which would give a constant logarithmic difference of 0.0151 for every degree. In this respect this change resembles another, otherwise totally different from it, namely, that between marble and hydrochloric acid, which varies by a like amount for equal differences of temperature. This relation is also exemplified by another pair of experiments in which 20 c.c. of nitric acid through which nitric oxide gas had been passed were made with water up to a constant volume of 100 c.c.

SERIES XXX.

Volume of solution = 100 c.c. Temperature, 21° 8'.
Ratio of nitrous to nitric acid = 1 : 10'2.

T.	C (observed). Grms.	C (calculated). $t=400$. Const. log = 1'7307.
0	1'3247	1'3451
30	1'2522	1'2512
60	1'1188	1'1175
90	1'0948	1'0978
150	0'9992	0'9781
180	0'9111	0'9275
210	0'8688	0'8799
240	0'8254	0'8405
270	0'7895	0'8010

SERIES XXXI.

Volume of solution = 100 c.c. Temperature, 31° 1'.
Ratio of nitrous to nitric acid = 1 : 10'34.

T.	C (observed). Grms.	T.	C (observed). Grm.
0	1'4432	190	0'8219
30	1'2868	220	0'7441
60	1'2045	250	0'6495
90	1'0720	270	0'6045
120	0'9679	300	0'5509

Percentage loss after

270° in series .. 58'05	Logarithm 1'76385
Do. do. .. 40'40	 1'60655
	Logarithmic differ- ence for 1° .. 0'0168

This difference is practically identical with those given above, though the masses of nitric and nitrous acids present were twice as great in the latter than in the former series of experiments.

(To be continued).

THE LAWS AND NATURE OF COHESION.

PART I.

By REGINALD A. FESSENDEN,
Prof. Elec. Engineering, Purdue University, Ind.
(Concluded from p. 207).

THE following is a Table of the metals and their Young's moduli. Col. I. contains the observed moduli taken from Sutherland's paper, and Col. II. contains the calculated values from the equation.

Equation III. Young's modulus = $\frac{78 \times 10^{12}}{(\text{atomic volume})^2}$
(corresponding to Equation I.).

Metals.	I.	II.
Iron	2000 × 10 ⁹	1560 × 10 ⁹
Copper	1220	1560
Zinc	930	920
Silver	740	750
Gold	760	750
Aluminium ..	680	690
Cadmium	480	465
Magnesium ..	390	395
Tin	420	295
Lead	190	235

There is only one metal which does not agree with theory, and that is tin (iron, of course, on account of its impurities does not, but we know that, as we obtain iron more pure, we find its rigidity less, so there is very little doubt but that if it were absolutely pure the agreement would be closer). But it is easy to show that the observed results for tin are wrong. For the rigidity is given as

136 × 10⁹ and the Young's modulus as 420 × 10⁹. Therefore if we represent Young's modulus by 1/a, then—

$$\frac{a}{2(a+b)} = \frac{136}{420}$$

Solving this we get $b = 0'55 a$. Therefore the bulk modulus—

$$\frac{1}{3(a-2b)}$$

is negative, and the more tin is compressed the larger it swells, a result which is absurd. This will emphasise the fact that the agreement between theory and experiment is as close as that between the experiments themselves.

It will be noticed that the ratio-rigidity to Young's modulus is about 28/78. Therefore, as $\pi/2(a+b) = 1/27$, Poisson's ratio for these metals is, on the average, 0'35. Therefore the bulk modulus = 1'1 times Young's modulus, which agrees with the only datum I find in Everett, i.e., Wertheim's figures for brass, which gives the ratio 9'48 : 10'2 = 1'08 very closely. All these moduli must contain the atomic volume to the same power, but this is not the case with the tensile strength; for, according to this electrostatic theory of cohesion, we may look at a wire as made up of thin discs, each disc consisting of a layer of atoms. The attractive force between any two such layers would vary inversely as the square of the distance between them and directly as the number of atoms in a layer. Combining these we find that it would vary as the fourth power of the atomic radius, or as (atomic volume)^{2/3}, making no allowance for the effect of temperature on the tensile strength. The following Table gives in Col. I. the observed tensile strengths, taken from Wertheim for wires 1 m.m. in diameter; in Col. II. the atomic volumes of the elements, raised to the 2/3-power; and in Col. III. the calculated tensile strengths as found by the formula.

Equation IV. Tensile strength = $638/(\text{atomic volume})^{2/3}$ in kilograms. for wires 1 m.m. in diameter.

Metal.	I.	II.	IV.
Iron	65	13'7	48 2000 (?)
Copper	41	13'7	48 1327
Platinum ..	35	17'8	36 1800 (?)
Zinc	15'77	19'3	33 690
Silver	29'6	22'2	29 1223
Gold	28'46	22'2	29 1313
Aluminium ..	18	23'2	27 898
Tin	3'40	41	15 504
Lead	2'36	47'8	13 600

Col. IV. contains the melting-points in degrees Centigrade from absolute zero. Here we have to deal with a much more complicated phenomenon than that of rigidity. Rigidity is simply a function of the cohesive force. The tensile strength of a substance depends not only on the cohesive force of the metal, but also on its ability to resist flow. If a metal did not flow before being pulled apart, there is no doubt but that its tensile strength would be proportional to the 2/3-power of the atomic volume. As, however, it does flow, and the amount of flow is not simply proportional to the diminishing of the cohesive force, we have to make a fresh allowance for it. In all the metals the melting-point is reached when the linear expansion has amounted to about 2 per cent. So when the cohesion has diminished about 4 per cent the atoms no longer hold the same relative positions, but one can slip in and take the place of another. So at equal distances from their melting-points only can the tensile strength be proportional to the 2/3-power of the atomic volume. Consequently this ratio can only hold good with substances which have approximately the same melting-point. On examining the Table it will be seen that as copper, gold, and silver have approximately the same melting-point, the ratio does hold good with them. The same with tin and lead. Aluminium and zinc, which should be, the one

slightly weaker, the other slightly stronger, than silver, have a melting-point about one-half that of gold and silver, and they have about half the strength at the temperature of comparison which they should have. The melting-point of iron and platinum is higher than that of gold or silver, and consequently their tensile strength is greater. The flow of a metal depends on two things, the cohesive force and the kinetic energy of the atoms. What function the flow is of the temperature, as reckoned in fractions of the temperature at which the substance melts, it is hardly worth while to go into now. If we suppose it directly proportional (though we may feel fairly certain it is not so simple a function) so that, at the same temperature, a metal melting at half the temperature that another does flows twice as easily, we get the following Table, where Col. I. contains the observed tensile strengths, and Col. II. the calculated ones:—

Metal.	I.	II.
Iron.. ..	65	74
Copper	41	48
Platinum	35	48
Silver	29.6	29
Gold	28.5	29
Aluminium	18	18
Zinc	15.7	16
Tin	3.4	5
Lead	2.36	4

I have not been able to find any data for the tensile strength of magnesium. Theory gives about 9 kilograms. for a wire 1 m.m. in diameter. It would be interesting to find if experiment confirms this.

If, then, we have met with a new phenomenon in a substance, and are able to show that a certain property already known to exist in the substance is capable of producing effects of the magnitude observed, and that the phenomenon obeys the same laws as it would if it were caused by the already known physical property, we are to a certain extent justified in supposing that this property is really the cause of the phenomenon in question, and in applying our knowledge still further. We have seen that the charges which we know the atoms have on them are able to give effects of the same size as those observed in experiments on tensile strength, and that the various moduli follow the same laws as they would if cohesion were an electrostatic effect, and we may now apply our formula to other and less-known phenomena.

The velocity of sound in a wire is given by the formula:—

$$\text{Velocity} = \left(\frac{\text{Elasticity}}{\text{Density}} \right)^{\frac{1}{2}}.$$

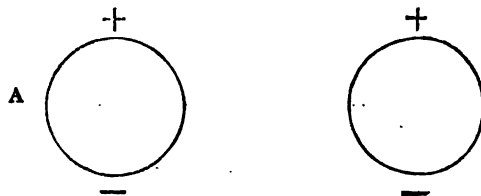
Elasticity here means Young's modulus, the formula for which, as we have seen, was constant $\div$ (atomic volume)², and atomic volume is atomic weight $\div$ density, so we have velocity of sound in wire =

$$= \left(\frac{\text{constant}}{\text{atomic weight} \times \text{atomic volume}} \right)^{\frac{1}{2}},$$

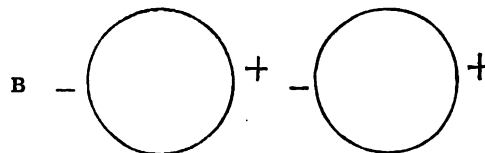
the constant being 78×10^{11} . The following table gives in Col. I. the velocities of sound in wires of a number of metals which have been tested, and in Col. II. the calculated velocities for these and for other metals which have not yet been tested.

	I.	II.	III.
Silver	2.61×10^4	2.7×10^4	100
Copper.. ..	3.56	4.1	110
Gold	1.74	1.9	136
Alumin.	—	5.1	200
Magnes.	—	4.8	275
Zinc	—	3.6	375
Cadmium	—	2.3	450
Tin	—	2.0	878
Lead	1.23	1.4	1300

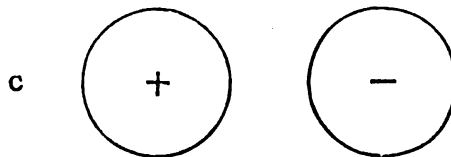
Col. III. gives the electrical resistance, silver being taken as 100, and it may be noticed that in any one group of metals the conductivity varies directly as the velocity of sound, and in passing from one group to another, by multiplying the conductivity by the valency we get proportionate values for all the metals. The same holds good for the heat conductivity. No close agreement can be expected here, for there are too many things to be taken into account. It is merely mentioned here because the fact of their being a relation between the velocity of sound and the conductivity for heat and electricity throws a light on the nature of these phenomena. This will form the subject of a separate paper. It may be asked *how* an electrostatic force can produce such effects. If the atoms are all similarly charged either + or - they would repel each other and not attract. The explanation is probably this: The atoms, if we may call them so, of electricity are not infinitely smaller than the atoms of matter. When an atom is neutral it does not mean that it has no charge, but that it has equal quantities of both kinds of electricity. The resultant effect of these charges on a body at a distance is zero; it behaves as if it had no charge, as shown below, in A.



If the atoms be brought close together there is a state of unstable equilibrium, and the effect is that either of the charges move on the surface of the atoms or the atoms themselves move so that the atoms attract each other, as in B. Consequently all atoms neutrally charged attract



each other. If nothing further happens, the attraction is simply cohesion. If, however, any third substance connects the two outside parts of the atoms, and so enables these parts to neutralise each other, we have chemical combination, and the two atoms when separated show opposite charges, as in C.



Whether we accept the electrostatic theory of cohesion or not, from the above tables of moduli, the following laws are evident:—

I. In any two metals the force of cohesion varies inversely as the square of the distance between the centres of their atoms.

II. In any one metal the force of cohesion varies inversely as the square of the distance between the centres of its atoms.

We may expect these facts to be of great use in the study of the properties of matter. For, knowing the size and weight of the atoms and the velocity with which they move, all that was wanting to enable us to calculate the behaviour of the atoms of matter, in the same way as we

do the motions of the planets, was a knowledge of the laws of the force which holds them together; and, from the evidence given above, I have no doubt that you will agree with me in saying that we have at least made a beginning in that direction.

A few words might be said about Poisson's ratio. It is, as I said, not fair to argue from the behaviour of cork or indiarubber that there is no relation between longitudinal extension and lateral contraction or between *a* and *b*. When we compress a cork, we are not compressing the substance which forms the cork any more than we are compressing a piece of paper when we crumple it up in our hand. A cork is like a dry sponge, and when we squeeze a sponge up in our hands we are simply doubling up the cell walls, not compressing the substance of the sponge. The only way in which we can determine the compressibility of cork is to soak it in ether or some substance which fills all its pores, and then subject it to hydrostatic pressure. In the same way, when we stretch indiarubber, or ivory, or jelly, the longitudinal extension of the piece of rubber is not in the least a measure of the longitudinal extension of the substance of the rubber. All such substances are made up of two parts; rubber, for instance, of a hard elastic skeleton, insoluble in most solvents, and of a soft plastic substance, soluble in many solvents, by use of which the two parts may easily be separated; similarly, ivory and jelly. Let us take a square cell as in Fig. 3, the walls of which are of elastic material and the contents an incompressible plastic substance. Suppose it to be extended till its length is 4 c.m. and its breadth and thickness each 2 c.m., as in Fig. 4. The total area of cell-wall is 40 square c.m., and the total volume of incompressible contents is 16 c.c. Imagine the cell to be released, it will regain its position as in Fig. 3, and form a cube of side 2.52 c.m. In this case, the volume being the same, the cell area will be 38.1 square c.m. So we find that by stretching the cell till its length was 60 per cent greater than before, we have only had to stretch the cell-walls 5 per cent. This gives us the explanation of the well-known fact that stretched rubber contracts when heated. For if we heat the cell shown in Fig. 4, the incompressible contents will expand and tend to make the cell walls take that shape in which they can hold the most. This is obviously that of the original cube, therefore the result will be a contraction.

Of course the formulæ derived from this theory of cohesion give us the means of calculating the physical properties of metals which have never been examined, or even discovered. For example, it shows us that we have at our disposal a metal far superior to any metal yet known, one which is stronger than iron, lighter than aluminium, and a better electrical conductor than silver. Aluminium, in spite of its lightness, is too weak mechanically, and too poor a conductor to be used in many cases. But this new metal is four times as strong as aluminium, and is twice as good a conductor of electricity. The metal referred to is glucinum or beryllium. All that is known about it is that it has an atomic weight of 9.1 and a density of 1.7 to 2, the exact figures not being known. But from these scanty data we can deduce the following figures:—

Metal.	Rigidity.	Tensile strength.	Conduc'ty.	Sp. gr.
Aluminium ..	250 × 10 ⁶	18 K. grms.	50	2.75
Silver ..	280	27	200	10.5
Iron ..	750	42.65	14	8
Calculated for glucinum ..	1300	65	105	2

We also see why diamond is so hard, and that there is only one other thing that might possibly scratch it, and that is a crystal of manganese. With the exception of glucinum, none of the other metals, either discovered or to be discovered, are likely to be any better than those we have now.

THE USE OF FLUORIDES IN THE MANUFACTURE OF ALCOHOL.*

By Dr. LEO BAEKELAND.

(Concluded from p. 204).

In another series of experiments wort was prepared in the same way, but after being cooled off to 30° C., 3 grms. of yeast per litre were added. This mixture was put in several bottles which were provided with a hydraulic stopper and which could be kept at a temperature of 30°. To the contents of some of these bottles a previous addition of fluoride had been made in quantities equivalent to 6 grms. per hectolitre of wort. After three days fermentation was complete in all the bottles, and the comparative analysis showed:—

	No fluoride.	Fluoride, (6 gr. per hectolitre).
Alcohol	6.4	7.2
Acidity (normal soda per 100 c.c.)	5.6	4.0

The proportion of alcohol in the above results is about 12.5 per cent higher in the sample where fluoride has been used. (See also Effront, "Action des acides minéraux dans la saccharification par le malt et la fermentation des matières amylacées," *Moniteur Scientifique*, 1890; Maerker, "Flusssäure verfahren," *loc. cit.*)

The specific action of fluorides on the development and activity of yeast cells has been the object of other interesting experiments. (See Effront, *Moniteur Scientifique*, November, 1891; also Maerker, *loc. cit.*) An addition of small quantities of fluoride, say in 30 m. grms. per 100 c.c., is favourable to the development or increase of the number of yeast cells. Larger quantities (70 to 150 m. grms.) decrease the formation of new yeast cells, and when as much as 250 to 300 m. grms. per 100 c.c. are used, the development of new yeast cells is practically interrupted. But even then, when such large quantities of fluoride are used, the ferment itself is not killed; it has merely suspended the reproductive faculties of the yeast cells, while their alcohol making action is still existent but with lessened activity. Furthermore, if such yeast heated previously with relatively large quantities of fluoride is brought into fresh wort containing no fluoride, it will at once resume its full vital properties, new yeast cells will be produced, and the alcoholic fermentation will be very energetic.

In some experiments small quantities of yeast (0.25 to 0.25 grm. per 500 c.c.) were added to sweet wort made with corn and left to develop with different quantities of fluoride, and afterwards the relative number of yeast cells was determined in each of the samples, with the following results:—

	Acidity (C.c. normal soda).	Relative number of yeast cells.
No fluoride	1.10	331
0.02 amm. fluor. ..	0.80	449
0.07 "	0.90	381
0.15 "	0.70	208

A certain quantity of each of these samples has been added to a fresh wort containing no fluoride (500 c.c. of each sample to 1 kilogr. of wort, 17.4 Sacch.), and after the fermentation was finished the quantity of alcohol produced by the sample was—

	Alcohol. Per cent.
No fluoride	4.1
0.02 grm. amm. fluor. ..	7.1
0.07 "	8.4 (1)
0.15 "	8.5 (1)

The above results show clearly that even by starting with a smaller number of yeast cells, more alcohol has been produced, and this is on account of the increased vital powers of these yeast cells after they have been under influence of fluoride.

* From the *Journal of the American Chemical Society*, xiv., No. 7.

The specific action of fluorides is not the same on all varieties of yeast. Four kinds of yeast have been especially examined in this direction:—

Saccharomyces	Cerevisiæ.
"	Pastorianus I.
"	Carlsberg.
"	Bourton.

By addition of 100 m.grms. of fluoride to 100 c.c. of liquid the following results have been observed:—

	Decrease of development of yeast cells by addition of 100 m.grms. fluoride.	Decrease in production of alcohol by addition of 100 m.grms. fluoride.
S. Pastorianus ..	34 per cent	41 per cent
S. Bourton ..	31 "	14 "
S. Carlsberg ..	25 "	13 "
S. Cerevisiæ ..	9 "	4 "

This shows that *S. Pastorianus* is most sensitive to an addition of 100 m.grms. fluoride, the quantity of alcohol decreases to 41 per cent of what can be produced without fluoride. *S. Bourton* and *S. Carlsberg* are less sensitive, but the most resisting of all is *S. Cerevisiæ*. By addition of 300 m.grms. of fluoride the production of new yeast cells is nearly completely stopped in the four varieties, but even then *S. Cerevisiæ* gives about three times as much alcohol as *S. Pastorianus* (see Table).

Name of yeast.	No. of sample.	Fluoride per 100 c.c. m.grms.	No. of yeast cells.	Alcohol, per cent.
Pastorianus I.	1	0	23	7.3
"	2	100	15	4.3
"	3	150	8	2.6
"	4	200	7	2.4
"	5	300	2	1.7
Bourton	6	0	32	7.9
"	7	100	22	6.8
"	8	150	20	5.8
"	9	200	10	4.1
"	10	300	3	4.0
Carlsberg	11	0	16	6.8
"	12	100	12	5.9
"	13	150	10	5.6
"	14	200	6	5.2
"	15	300	2	2.3
Cerevisiæ	16	0	22	7.1
"	17	100	20	6.8
"	18	150	11	5.2
"	19	200	4	4.9
"	20	300	2	4.5

The difference in the resisting power of these four varieties of yeast to the action of fluorides can be used to separate one from another. For instance, if a mixture of equal parts of *S. Pastorianus* and *S. Bourton* (whose cells are easily to be distinguished under the microscope) is kept during 72 hours in a wort containing 300 m.grms. of fluoride per 100 c.c., and afterwards transferred to a wort containing no fluoride, where they are allowed to ferment during 48 hours, and if these operations are repeated three times, it is possible to eliminate entirely all yeast cells of the *Pastorianus* variety.

It is to be noted as an important fact that yeast can be kept for more than six months with an addition of 200 to 300 m.grms. of fluoride per 100 c.c. Even after this time the yeast cells have proved to be in an excellent state of preservation, and when brought afterwards in a wort without fluoride they developed rapidly and produced a splendid fermentation.

The practical results which have been obtained in distilleries, after Effront's process have fully demonstrated

the remarkably useful properties of fluorides. In Europe nearly all important distilleries have adopted the process, and their reports have been very favourable. In general an increase from 8 to 10 per cent in the yield on alcohol has been obtained, and a more steady and more complete fermentation has been noticed. The production of lactic and butyric acid has been reduced to a minimum. The quality of alcohol has also improved, and this is probably due to the prevention of secondary fermentations. The odour and taste of such alcohol is very similar to that of ordinary alcohol that has been filtered over charcoal.

From the beginning when the fluoride process was introduced into distilleries, special experiments have been made in order to see if the presence of small quantities of these salts in the slops or wash did not have unhealthy effect on the cattle using such food. Dr. Tappeiner (*Zeit. des Landwirth's Vereins in Bayern*, 1890) has published some interesting laboratory experiments which show clearly that not the smallest difference has been observed in the use of such slops, either in the composition of the milk nor the general conditions of the animals fed upon it.

Since then practice has entirely confirmed these conclusions. The slops produced from distilleries working with fluoride is far less acid than usual and is remarkable for its keeping qualities. While, usually, slop becomes acid very quickly, it will, on the contrary, keep for weeks without much alteration if fluorides are used. Its taste is sweeter also, and this is probably the reason why in some cases where the fluoride process has been introduced, it took the cattle a few days before being accustomed to this taste. It should be reported, however, that in one case when the slop was used over again in the mashing process the fluorides seemed to accumulate in it, and therefore it is thought advisable not to use the same slop more than twice if it has to be used afterward for feeding purposes.

CORRESPONDENCE.

A NEW SILVER ORE.

To the Editor of the Chemical News.

SIR,—In reply to Mr. Roger's statement with respect to my note upon a new silver ore, I am perfectly aware of the exhibits he mentions, and of the difference existing between mine and the same. Perhaps Mr. Rogers will read my note again; he will then see that I stated nothing definitely as regards the manufacture of porcelain from the same, which he so pointedly asserts.—I am, &c.,

HENRY N. WARREN.

Uranium.—It is announced that a vein of silver containing a high percentage of uranium has been discovered in South Africa, on a farm belonging to the White Bank Silver Syndicate.

Diagnosis of α - and β -Naphthol.—Herr Verhassel (*Journ. der Pharmacie d'Anvers*) proposes the following reactions:— α -Naphthol in an aqueous solution gives a violet colouration with solution of chloride of lime and of potassium ferrocyanide; with potassium ferricyanide a brown colouration; with ammonia the liquid remains colourless. In an alcoholic solution it gives with ferric chloride a violet precipitate. β -Naphthol in a watery solution gives with chloride of lime a greenish yellow, with potassium ferrocyanide a light yellow, with ferricyanide a greenish yellow, and with ammonia a greenish colouration. In an alcoholic solution it gives a greenish colouration and precipitate with ferric chloride.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 15, October 10, 1892.

On December 7th next the University of Padua celebrates the 300th Anniversary of the day when Galileo entered upon his chair at the University.

Novel Preparation and Photometry of Phosphorescent Zinc Sulphide.—Charles Henry.—According to the author we may obtain in one operation several kilos. of a fine phosphorescent zinc sulphide by treating a perfectly neutral solution of pure zinc chloride with ammonia, re-dissolving the precipitate in an excess of ammonia, precipitating the ammoniacal zinc oxide completely, though without the least excess, with hydrogen sulphide, heating to whiteness with suitable precautions in a crucible of refractory clay placed within a graphite crucible lined with charcoal, washing perfectly the amorphous zinc sulphide and drying it with exclusion of every impurity. Contrary to the alkaline earthy sulphides, zinc sulphide becomes phosphorescent only when perfectly pure. The author finds the mean luminous intensity of this phosphorescent sulphide (5.432 grm. in a tube 10 m.m. in diameter and 42 m.m. in height) = 0.000215 of a normal candle at the distance of 1 metre.

On Pyrogallol Antimonites.—H. Causse and C. Bayard.—The acid antimonite, $C_6H_5O_2 + SbO_3H_3$, forms minute crystals insoluble in water, alcohol, benzene, and chloroform, but soluble in sulphuric, nitric, and hydrochloric acids. The neutral antimonite, $C_6H_5O_3Sb$, differs from the acid compound merely in composition.

On the Tartaric Ethers.—P. Freundler.—The author has obtained the methylic, ethylic, normal propylic, and isobutylic derivatives of the diacetyltartaric, dipropionyltartaric, and dibutyryltartaric (normal butyric acid), as well as the normal butylic ether of diacetyltartaric acid; in all thirteen compounds, all new except the methyl, ethyl, propyl, and isobutyl diacetyltartrates, which have been already studied, but the rotatory power of which have been determined only in solution.

New Method of the Production of Bricks used in Certain Parts of Central Asia.—E. Blanc.—The method in question is used in the western parts of Mongolia, where the extreme and rapid alternations of temperature disaggregate most natural rocks as well as bricks burnt in the ordinary manner. The kiln has the form of a vertical cylinder surmounted by a dome at the top of which is a rather wide hole, which remains open during the first part of the process. Three draught chimneys built inside the furnace open outwards at the height of the dome, and are closed with clay at the beginning of the operation. The fire is kept up for three days, a dry herb, *Alhagi camelorum*, being used as fuel. The third day the hole at the top of the dome is gradually reduced in diameter by means of blocks of moistened clay; the flame is let die down, and the opening is closed with a cover of wet felt forming a kind of bag, which is filled with sand kept constantly wet. The three lateral apertures are unstoppered, and the flame is kept as high as possible for four days. The draught is thus reversed, the steam which fills the interior of the kiln is superheated, and attains a higher pressure than that of the external air. The bricks, which on the third day were of a light red, take a uniform dark grey colour, and become sonorous and very hard, resembling in appearance certain trachytic rocks.

Process for Ascertaining the Purity of Coprah Oil and Palm Oil.—Ernest Milliau.—This paper will be inserted in full.

The Volumetric Determination of Alkaloids.—L. Barthe.—This paper will be inserted in full.

The Part played by Spermine in Intra-Organic Oxidations.—Alex. Poehl.—This paper is rather medical than chemical in its character.

Zeitschrift für Analytische Chemie.
Vol. xxxi., Part 4.

Apparatus for the Development of Gases.—W. Reatz.—The apparatus cannot be intelligibly described without the figure.

A Glass Tripod.—W. Reatz.—A recommendation to make tripods of glass tubing instead of rods.

Action of Barium Peroxide upon Metallic Salts.—W. Kwasnik (*Archiv. der Pharmacie*).—Not merely potassium ferricyanide but a series of other salts act upon barium peroxide so as to liberate oxygen. The salts of the alkalies and alkaline earths do not liberate oxygen, magnesium salts and also those of zinc and cadmium slightly. The salts of nickel, cobalt, iron, manganese, chrome, and aluminium produce a powerful development of gas. The hydroxides of the metals are formed, and half the oxygen of the barium peroxide is liberated. In the salts of the lower oxides of the last group the development of oxygen ensues in two phases. There occurs firstly oxidation, and gaseous oxygen is afterwards liberated. Cupric salts give at once a brisk discharge of gas. Salts of mercury, silver, and gold liberate two atoms of oxygen for each mol. of barium peroxide, and the metallic salts are reduced. Platinum forms an exception to the behaviour of the above-named precious metals. On employing platinum chloride hydrochlorate there is formed a soluble compound resembling potassium-platinum chloride. The double chlorides of platinum and an alkaline earthy metal do not act upon barium peroxide. Platinum chloride ($PtCl_4$) and silver-platinum chloride—



are decomposed with elimination of platinum or platinum and silver. Barium peroxide yields oxygen not merely with soluble metallic compounds, but also with those insoluble in water, though the action is slower.

Determination of the Specific Gravity of Solids.—L. Liebermann (*Math. Naturwissen Berichte aus Ungarn*).—A known quantity of the substance in question is to be precipitated in a vessel of known weight and volume, filled up to the mark with water, weighed, and the specific gravity of the filtrate is determined after filtration. The author recommends pycnometers where the top is ground to fit on not into the recipient.

On Glass and the Influence of its Composition upon its Properties.—A series of papers.

Comparison of Mercurial Thermometers.—Papers by H. F. Wiebe and W. Pomplun (*Zeit. Instrumentenkunde*).—Wiebe's device is not described. Pomplun's apparatus depends on the principle of maintaining temperatures constant by means of a few liquids which are not affected in their composition by prolonged boiling, their points of ebullition being modified by alterations of pressure.

Execution of Reactions at High Temperatures and Pressures.—W. Hempel (*Ber. Deut. Chem. Gesell.*).—The author obtains the heat in the interior of the apparatus by electrical agency, whilst the external walls are kept cool by means of cold water. The arrangement approximates to the electric furnace of W. Siemens.

Characterisation of Flame.—N. Teclu (*Journ. Prakt. Chemie*).—This paper requires the accompanying figure.

A Vacuum Exsiccator capable of being Heated.—J. W. Brühl (*Ber. Deut. Chem. Gesell.*).—A transportable air-pump plate contains beside the middle aperture, which serves for evacuation, two lateral perforations

through which tubes from the source of heat are introduced.

Development of Gases.—C. G. Moor.—From the *CHEMICAL NEWS*.

New Weighing-Bottle.—C. Mangold.—This note requires the accompanying figure.

New Apparatus for the Extraction of Fats.—J. T. Willard and G. H. Faigler (*Journ. Anal. App. Chem.*).

Pipette for Mercury.—V. Dvorak (*Zeit. fur Instrumentenkunde*).—Both these papers require the appended illustrations.

New Method for Producing Hydrobromic Acid.—G. S. Newth.—From the *CHEMICAL NEWS*.

New Methods of Quantitative Analysis.—A. Baumann.—This memoir is in the course of insertion.

Detection of Salicylic Acid in Salicylaldehyde and in Salicylic Methyl ester.—A. Schneegans and J. E. Gerock (*Journ. d. Pharm. von Elsass-Lothringen*).—Already inserted.

Reagent for Guanidines.—O. Prelinger (*Monatshefte fur Chemie*).— α -Triphenylguanidine picrate is very sparingly soluble in cold water. Aqueous solutions of α -triphenylguanidine are at once precipitated by picric acid. Since phenylguanidine and methylguanidine behave in a similar manner with picric acid, the author considers that it may be considered a general reagent for the guanidines.

Ultimate Analysis of Nitrogenous Substances.—Clemens Gehrenbeck and Felix Klingemann have made communications on this subject in the *Ber. Deut. Chem. Gesell.*

Oxidation of Organic Compounds by Potassium Permanganate.—R. Benedikt and J. Neundörfer (*Chem. Zeit.*), and C. Micko (*Zeit. Oesterr. Apoth. Vereins*).—The two former authors studied the conditions under which ethyl alcohol is converted into oxalic acid by permanganate, but without success. Micko endeavoured to determine malic acid by complete oxidation with permanganate, but he did not arrive at any satisfactory results.

Separation of Malic Acid from the Succinic, Citric, and Tartaric Acids.—C. Micko (*Zeit. des Oesterr. Apoth. Vereins*).—This paper will be inserted in full.

Determinations of Tannin.—A. Klinger and A. Bujard (*Zeit. fur Angew. Chemie*) come to the same conclusion concerning the Gantler process as do Von Schröder and Passler. The consumption of permanganate by tanniferous solutions after the tannin has been precipitated by hide-powder must by no means be neglected. If this point is overlooked, an error of 5 per cent in excess is obtained in case of oak bark. As the hide-power generally contains soluble organic substances, their consumption of permanganate must be ascertained and deducted.

Determination of Glycerin in Wine.—Th. Lecco (*Chem. Zeit.*).—This paper will be inserted in full.

Balance for Determining Percentage Changes in Weight during Evaporating, Drying, Roasting, &c.—G. W. Barth (*Zeit. Angew. Chemie*).—This apparatus consists of a beam resting on a pillar. One half of the beam is divided into 100° , and on it is a movable capsule-shaped counterpoise. To the other arm of the beam there is attached a scale pan for receiving the substance in question. The weight of the scale pan is compensated by means of a weight fixed to the graduated arm; the counterpoise is moved to 100° , and the substance to be examined is placed in the scale pan. The capsule-shaped counterpoise is loaded with shot, and the balance allowed to play. The scale pan with the substance in question is now exposed to the desired agency, generally heat. If there occurs a loss of weight, equilibrium is restored by displacing the capsule-shaped counterpoise, and the percentage of the substance which has not been volatilised can be read off from its position.

A Calorimeter.—H. Pellet and A. Demichel (*Bull. de l'Assoc. Belge des Chimistes*).—The apparatus consists of two long horizontal tubes laid side by side, one of them serving to receive the paler comparative solution. To the other tube is fixed a relatively large funnel, by means of which 10 or 20 c.c. of the darker solution may be introduced. By adding measured quantities of water and mixing by forcing air into it, the darker solution is diluted until the colour in both is equal in shade.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 14.

Preparation of Basic Zinc Acetate in Crystalline Needles.—A. Terreil.—The author obtains this substance by the prolonged action of dilute nitric acid. The compound obtained corresponds to the formula $5(\text{ZnO})\text{NO}_5, 5(\text{HO})$.

Residues from the Preparation of Propylenic Glycol.—L. Raisonier.—The action of soda upon glycerin at elevated temperatures yields propylenic glycol mixed with a certain quantity of alcohols. From this mixture the author has separated ethylic and allylic alcohols. Methyl alcohol may be considered as the chief product of the reaction. Propylic alcohol was not obtained.

MEETINGS FOR THE WEEK.

WEDNESDAY, Nov. 2nd.—Society of Public Analysts, 8. (1) "Note on a Sample of Poor, but undoubtedly Genuine Milk," by C. W. Heaton. (2) "Composition of an Abnormal Sample of Milk," by Alfred Smetham. (3) "Note on a case of Abnormal Milk," by Dr. Bernard Dyer.

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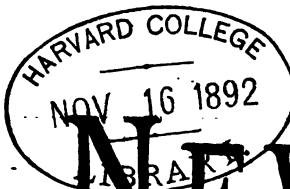
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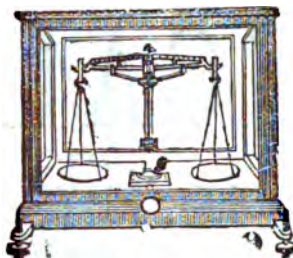
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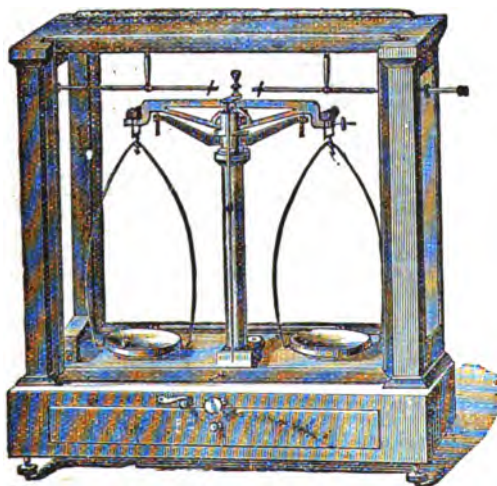


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THE CHEMICAL NEWS.

VOL. LXVI., No. 1719.

PRELIMINARY NOTE ON THE ACTION OF DRY AMMONIA-GAS ON SULPHATES.*

By W. R. HODGKINSON and C. C. TRENCH, Col. R.A.

VERY little appears in chemical literature as to the action of really dry ammonia-gas on salts at an elevated temperature. Some chlorides are said to be reduced, others to yield nitrogen compounds when heated with ammonia, but little or nothing seems to be known respecting the action with sulphates.

The experiments were undertaken to ascertain (1) to what extent, if any, sulphates were reduced by ammonia at temperatures below that at which the sulphate itself decomposes; and (2) whether nitrogen compounds (nitrides) could be formed.

All the work has been quantitative as far as possible. After a number of preliminary experiments the reactions were carried on in a wide glass tube so arranged that it could be heated in an air-bath to a definite temperature when required or by the naked flame. The substance was contained in a boat of platinum or porcelain as the case demanded, which with its contents was weighed before and after the action. The ammonia was dried by passing first over potassic hydrate, and then over a considerable quantity of freshly ignited lime.

As water is, however, certainly one product of the mutual action of ammonia and sulphates, this drying is perhaps not an essential precaution. To catch volatile products the tube was drawn out to about 50 c.m., and either dipped into water or ended in a dry flask externally cooled.

General Results.

The preliminary experiments showed that some metallic sulphates were entirely reduced by heating with ammonia. Silver, mercury, and bismuth behaved in this manner. Water, and what at first appeared to be ammonium sulphite, were the only products of a volatile nature. The actions were completed at the melting-point of zinc.

Lead sulphate required a high temperature before any action was visible, and the salt was not completely decomposed by heating for an hour at a red heat. A little lead sulphide was produced. Thallium sulphate acted in a similar manner, but more sulphide was formed.

Ferrous sulphate (dry) precipitated by addition of strong acid to the concentrated water solution of FeSO_4 , and then dried *in vacuo*, ordinary crystallised ferrous sulphate, and the ammonium ferrous sulphate were all reduced to metallic iron, which, however, contained 1 to 2 per cent of sulphur. The sulphates of zinc, magnesium, cobalt, nickel, manganese, and chromium were remarkably alike in their behaviour.

In all these cases the quantity of material left in the boat after heating corresponded very closely with that required if a sulphide of the form MS_2 had been formed. As a matter of fact, the residue consisted of a mixture of the sulphide and oxide in nearly molecular proportions. No nitride has as yet been obtained.

As far as the volatile portion is concerned, the main bulk in all cases appeared at first to be ammonium sulphite. No trace of sulphate was found. In the hot tube in which the reaction was carried on, the substance which condensed was for the most part ammonium thionamate, $\text{NH}_3\text{OHSONH}_2$. Where this came in contact with water

in the condensing flask or with moisture in the cooler parts of the tube, ammonium sulphite was of course formed.

Undoubtedly the most interesting salt examined is cupric sulphate. Either dry or with crystal water, the salt absorbed much NH_3 , and then melted below 200° , turned black, and as the temperature rose appeared to boil, and finally at somewhere about 400° began to decompose with incandescence, leaving almost pure metallic copper.

The comparatively low temperature at which an action was observable in the case of copper sulphate suggested the possible formation of a hydrazin compound.

The white sublimate was therefore examined for its reducing power on Fehling's solution and silver nitrate. As thionamate reduces both silver and copper solutions when alkaline, some of the white sublimate was distilled from potassium hydrate solution and the distillate collected in dilute sulphuric acid. This solution also reduced Fehling's solution. There is little doubt but that hydrazin is present along with the thionamate sublimate, but the quantity is small, and in several experiments could not be detected at all, probably on account of the temperature being too high when the ammonia comes in contact with the sulphate.

We are continuing this work in the hope of getting an easy method for the production of hydrazin compounds.

ON THE VOLUMETRIC DETERMINATION OF THE ALKALOIDS.

By L. BARTHE.

I HAVE ascertained that the best known alkaloids of vegetable origin are without action upon phenolphthalein, which they leave in the state in which it comes into contact with them; colourless if the medium is neutral or acid, rose coloured if it has been rendered alkaline by a mineral base. Such are quinine, cinchonine, cinchonamine, cinchonidine, quinine, morphine, codeine, cocaine, aconitine (amorphous or crystalline), strychnine, brucine, serine, veratrine, pilocarpine, duboisine, spartein. On combining this observation (made, I believe, for the first time) with the well-known property of the vegetable bases to turn red litmus blue, I have founded a general method for the volumetric analysis of the alkaloids.

If certain vegetable principles, hitherto regarded as alkaloids, do not react appreciably with phenolphthalein and litmus, it is doubtless because their properties are still imperfectly known, and that their chemical functions require accurate determination. For instance, narcotine, which, according to Picot and Flückiger, can scarcely be regarded as an alkaloid and which is without action upon phenolphthalein, litmus, and atropine, which with these substances behaves like a weak acid.

However it may be, the alkaloid to be determined must be brought to the condition of a soluble salt by means of a mineral acid, e.g., sulphuric acid, either in water or in a slightly alcoholic solution. An excess of acid does not prevent the reaction, but on the contrary rather promotes it. The presence of any salt of the alkaline or earthy bases, and even of a certain number of the heavy metals (e.g., zinc), has no effect upon the process.

The following method of operation is very easily applicable to the determination of the alkaloids above mentioned, and also of the acids with which they may be combined.

Determination of the Acid.

We introduce into a beaker of Bohemian glass 1-1000 part of an equivalent of the alkaloid or of a salt of the alkaloid, adding 10 c.c. of decinormal sulphuric acid in case of a salt, or 20 c.c. in case of a free alkaloid. We add 20 c.c. of neutral alcohol at 90 per cent, and three or four drops of an alcoholic solution of phenolphthalein.

* Read before the British Association, Edinburgh Meeting, 1892.

All the salts of the alkaloids dissolve in this acid alcoholic liquid. We then pour in decinormal potassa until there appears a faint rose-coloured tint of phenolphthalein. The number of c.c. of decinormal potassa used expresses all the acid, free or combined, existing in the mixture. The rose-tint of phenolphthalein appears only when all the alkaloid is in the free state in the liquid; as a transparent solution if the alkaloid is soluble in weak, neutral alcohol, or as a precipitate if it is insoluble. We have thus a mixture indifferent to phenolphthalein, but alkaline to litmus in consequence of the liberation of the alkaloid.

Determination of the Alkaloid.

Into a second beaker of Bohemian glass we introduce 1-1000 of an equivalent of the alkaloid, or of a salt of an alkaloid, with 10 or 20 c.c. of decinormal sulphuric acid, and then some drops of a sensitive tincture of litmus. The colour is then rendered blue again by means of decinormal potassa. The number of c.c. of the alkaline liquid employed in this second saturation represents merely the free acid. If this number is subtracted from the figure which in the foregoing operation measures the entire acid, it expresses exactly the quantity of sulphuric acid combined with the alkaloid in the state of a basic salt, and consequently the weight of the alkaloid itself. It is, in fact, sufficient to multiply the remainder from the subtraction by 1-10000 of the equivalent of the alkaloid in question. The factors are evidently:—

For anhydrous quinone	0.0324
„ cinchonine	0.0294
„ codeine (H ₂ O)	0.0317
„ morphine (H ₂ O)	0.0303

—*Comptes Rendus*, vol. cxv., p. 512.

PURITY OF THE OIL OF COPRAH AND OF PALM-OIL.

By ERNEST MILLIAU.

At from 30° to 31° the oil of coprah, if pure, is soluble in twice its volume of absolute alcohol. At the same temperature palm oil is soluble in four times its volume of absolute alcohol. If mixed with sparingly soluble vegetable oils or animal fats to the extent of 1-20th, or less, both become almost insoluble in the same quantity of absolute alcohol, the solvent action of which does not occasion a fractionated separation of the component parts. The mixture has acquired a solubility which is peculiar to it, and which does not depend on the proportions of soluble and insoluble fatty matters of which it is composed.

These differences of composition enable us to determine with precision the purity of these solid oils, a chemical analysis of which often gives uncertain and even contradictory results, especially for slight admixtures.

Method of Operation.

First Process.—We shake up for one minute, in a test-tube graduated in c.c., 20 c.c. of the oil under examination with 40 c.c. of alcohol at 90°. This indispensable preliminary treatment may give certain indications. Alcohol at 95° absorbs a certain quantity of the neutral fatty substances, and the oil itself dissolves from 15 to 20 per cent of alcohol. The solvent power of the oil decreases appreciably on the addition of insoluble oils, whilst that of alcohol increases by the addition of oils soluble in alcohol at 95°, such as castor and resin oils,—oils which may then be easily characterised by their very distinct chemical and physical properties.

Second Process.—In a test-tube graduated in c.c. we treat 5 c.c. of the oil of coprah (previously washed with alcohol at 95°) with 10 c.c. of absolute alcohol, and we place the tube in a water-bath heated very exactly to from

30° to 31°. After some moments the tube is taken out, shaken very briskly for thirty seconds and returned to the water-bath. Pure coprah oil dissolves entirely, and the alcoholic solution is perfectly clear.

Coprah oil mixed with insoluble oils (the commonest sophistication), arachis, sesame, cotton, maize, &c., does not dissolve appreciably, and forms a turbid mass with the absolute alcohol, from which it quickly falls in fine drops to the bottom of the tube, where it collects. Oil of coprah containing palm-oil is precipitated when the proportion of the mixture reaches 20 per cent. Below that limit the mixture remains turbid.

The verification of palm-oil is effected in the same manner, using 20 c.c. of absolute alcohol instead of 10 c.c., and operating always upon 5 c.c. of oil at the temperature of 30° to 31°.

Five c.c. of palm-oil containing 20 per cent of coprah or upwards dissolves in 15 c.c. of absolute alcohol; in the same proportions the pure oil does not completely dissolve and the mixture remains turbid. The purity of coprah and palm-oil cakes is found by extracting a sufficient quantity of oil by means of any solvent and treating in the same manner.—*Comptes Rendus*, vol. cxv., p. 517.

QUANTITATIVE DETERMINATION OF LEAD.

By LUDWIG MEDICUS.

In operating upon galenas the author adopts the following method:—After converting the lead into a chloride he dissolves the lead chloride in potassa-lye, and passes a current of carbonic acid through the solution for two hours. The precipitated carbonate is filtered off, washed, dissolved in nitric acid, and the lead is precipitated electrolytically as peroxide.

He attempted also to precipitate the lead from the alkaline solution as peroxide by means of bromine. He succeeded best in the following manner:—The chloride is dissolved in potassa-lye; the solution is poured into a flask closed by a cork, with two perforations for the introduction and the escape of gas. A slow current of gaseous bromine is passed through the entrance tube above the liquid, which is gently heated. The bromine is readily absorbed and the lead is gradually deposited as peroxide. The filtration is best effected by exhaustion through finely elutriated asbestos placed between two discs of asbestos paper.—*Ber. Deutsch. Chem. Gesell.*, vol. xiv., p. 2490.

NEW METHODS FOR QUANTITATIVE ANALYSIS.*

By A. BAUMANN.

(Continued from p. 213).

Determination of Combined Iodine and Iodic Acid.

With the possibility of determining free iodine accurately in a gas-volumetric manner, it becomes possible to effect a determination of combined iodine in iodides and iodates. It is easy to eliminate iodine from its combinations in a free state.

For determining iodine in iodides we distil the sample with acid ferric sulphate, receive the liberated iodine in a solution of potassium iodide, and shake up the distillate with alkaline hydrogen peroxide in the manner above described. It is preferable to make up the distillate to a known volume (100 c.c.), and effect the determination in a part (50 c.c.), so that a check analysis can be effected with the rest.

In order to determine iodic acid we add to the liquid

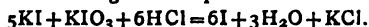
* *Zeit. für Angew. Chemie und Zeit. für Analytische Chemie*

containing the iodate potassium iodide, and then a slight excess of sulphuric or hydrochloric acid, and determine the liberated iodine according to the gas-volumetric method.

Like iodic acid, other substances which liberate iodine from potassium iodide, without the use of sodium thiosulphate, may be determined much more simply and quickly gas-volumetrically than by titration. Baumann, in conjunction with Kestler, is still engaged with experiments in this direction.

Determination of Free Acids—Acidimetry without Normal Alkali.

F. Mohr expressed the opinion that free acid might be determined by means of potassium iodide and potassium iodate, since even weak acids liberate iodic acid, which, then in contact with potassium iodide, sets free iodine. For each atom of hydrogen in the acid an atom of iodine is liberated according to the equation—



The free iodine is then determined in the usual manner.

This method, which was not able to establish itself, was again brought into notice by Kjeldahl, when he made known his new method for the determination of nitrogen in organic substances. In a subsequent communication he returned to his proposal and recommended to render the solution of sodium thiosulphate more permanent by dissolving the salt in water which has been recently boiled and preserving the solution from light and from carbonic acid. The thiosulphate solution is conveniently adjusted to a solution of iodine of known strength, or, as proposed by Knublauch, we prepare a solution of pure ammonium sulphate (1 grm. in 100 c.c.), and subject 10 c.c. of this solution to distillation with potassium-lye, having a known quantity of acid in the receiver. The standard of the thiosulphate solution is found in the latter case by difference if we take a quantity of acid equal to that used in the distillation, and mix the distillate with potassium iodide and potassium iodate, and in both cases determine the liberated iodine with the solution of thiosulphate.

Standardising the solution of thiosulphate for normal acid directly by determining the iodine liberated by the latter in a solution of potassium iodide and potassium iodate yields no absolutely accurate values, since in dilute acids the reaction only proceeds gradually. The same quantity of iodine which in dilute solutions separates only after some time, depends on the dilution of the liquid and increases on further dilution. It is hence to be recommended to use in titration always an equal volume of liquid, although the fault occasioned by this retarded separation of iodine is always very trifling.

In determining ammonia by distillation Kjeldahl recommends the excess of normal acid to be titrated back in the following manner.

After completing the distillation the distillate is diluted with water to 100 c.c., since, according to what has been said, the volume of the liquid is important, and there are then added 10 c.c. of a 5 per cent solution of potassium iodide, starch paste, and 2 c.c. of a four per cent solution of potassium iodate.

For preparing the starch paste Kjeldahl digests potato starch for a week at the common temperature with dilute hydrochloric acid, washes by decantation, and dries between filter-paper. Starch thus treated, if heated, yields a solution which keeps unchanged if saturated with sodium chloride.

On the determination of acids and bases, especially ammonia, by means of iodine and thiosulphate, E. Pfüger has communicated an elaborate investigation. Pfüger determines the effective value of the thiosulphate solution by mixing 10 c.c. of sulphuric acid, 1 c.c. of which corresponds to 0.001 grm. of nitrogen with 1 c.c. of a 20 per cent solution of potassium iodide, and 1.3 per cent of a 4 per cent solution of potassium iodate. The thio-

sulphate solution is then added until the colour produced by the free iodine has disappeared. Pfüger rejects the use of starch paste in titrations, as it exerts a disturbing influence on the result. If a very dilute solution of iodine is coloured faintly blue with a small quantity of dilute starch paste, and is then mixed with more starch paste, the colour of the liquid often disappears. Pfüger ascribes this phenomenon to the fact that nearly all commercial starch contains a nitrogenous body, probably albumen, which eliminates the iodine from the starch iodide.

(To be continued).

THE CONDITIONS OF THE FORMATION AND DECOMPOSITION OF NITROUS ACID.*

By V. H. VELEY, M.A.

(Concluded from p. 217).

Nitrous Acid from Nitrogen Peroxide and Water.

ABOUT 1 to 2 c.c. of nitrogen peroxide were slowly added to 50 c.c. of water, the liquid being kept continually stirred; after the mixture had become uniform the volume was made up to 100 c.c. as before. By this means a dilute solution of nitrous and nitric acids was obtained. The method of experiment was conducted as usual.

SERIES XXXII.

Temperature, 21.8°. Nitrous acid present after complete admixture = 1.0663 grms. Nitric acid present after complete admixture = 2.3544 grms. Ratio of nitrous to nitric acid = 1 : 2.12.

T.	C (observed). Grm.	C (calculated). <i>t</i> = 1030. Const. log = 1.9819. Grm.
		Grm.
0	0.9181	0.9292
30	0.9151	0.9049
60	0.8952	0.8801
90	0.8597	0.8560
120	0.8373	0.8341
150	0.8171	0.8129
180	0.7819	0.7927
210	0.7618	0.7718
240	0.7538	0.7553
270	0.7381	0.7380

The Table below contains the results of another set of experiments with a more dilute solution.

SERIES XXXIII.

Temperature, 21.8°. Nitrous acid = 0.7292 grm. Nitric acid = 1.5457 grms. Ratio = 1 : 2.02.

T	C (observed). Grm.	C (calculated). <i>t</i> = 500. Const. log = 1.5587. Grm.
		Grm.
0	0.7292	0.7247
30	0.6811	0.6830
60	0.6401	0.6464
90	0.6166	0.6279
120	0.5843	0.5840
150	0.5570	0.5543
210	0.5095	0.5080
240	0.4856	0.4892
270	0.4736	0.4702
300	0.4502	0.4525

The greatest difference between the observed and calculated results is shown in the first two experiments, but this can in part be accounted for by the difficulty experienced in introducing the nitrous acid solution into the permanganate before that some of the liquid was projected from the measuring vessel by the rapidly evolved nitric oxide gas. The above three series of experiments show

* A Paper read before the Royal Society, June 2, 1892.

SERIES XXXIV.

Temperature, 31.8°. Nitrous acid = 2.4557. Nitric acid = 2.2571. Ratio of nitrous to nitric acid = 1:0.93.

T.	C (observed).		C (calculated). $t=160$. Const. log = 1.5692.	
	Grms.		Grms.	
0	2.2321		2.3180	
30	1.9764		1.9077	
60	1.6981		1.6858	
90	1.4778		1.4833	
165	1.1924		1.1413	
180	1.1081		1.0937	
210	0.9986		1.0024	
240	0.9010		0.9271	

that whether the nitrous acid produced from nitrogen peroxide and water is of a concentration of 0.45 per cent, or five times that amount, the rate of decomposition is in accordance with the mathematical formulæ given, since, as it happened by chance, the Series XXXII. to XXXIV. were continuous as regards the masses of nitrous acid contained therein.

Nitrous Acid from Nitrous Fumes and Water.

When nitrous fumes from arsenious oxide and nitric acid are passed into water at ordinary temperatures of 12 to 15°, their absorption is apparently very incomplete; a liquid is obtained nearly colourless, and containing 1 to 2 per cent of free nitrous acid. This solution gives off bubbles of gas very freely, especially when poured from one vessel to another, thus recalling to mind the behaviour of solutions of hydrogen peroxide. This very rapid evolution of gas introduced, as explained above, unavoidable errors in the method of experiment adopted; there is therefore not so complete an accordance between the observed and calculated values as in the other series of experiments.

SERIES XXXV.

Temperature, 31.7°. Nitrous acid = 0.7685 gram. Nitric acid = 0.6753 gram. Ratio of nitrous to nitric acid = 1:0.88.

T.	C (observed).		C (calculated). $t=160$. Const. log = 1.0927.	
	Grm.		Grm.	
0	0.7685		0.7697	
60	0.5665		0.5628	
90	0.4828		0.4953	
170	0.3898		0.3752	
200	0.3501		0.3439	
230	0.3342		0.3174	
260	0.2963		0.2948	

The rate of decomposition is nearly identical with that of Series XXXIV., conducted at the same temperature, and in which the ratio of nitrous to nitric acid was also nearly identical.

SERIES XXXVI.

Temperature, 19.8°. Nitrous acid = 1.1789 grms. Nitric acid = 0.3973 gram. Ratio of nitrous to nitric acid = 1:0.34.

T.	C (observed).		C (calculated). $t=160$. Const. log = 1.2561.	
	Grms.		Grms.	
0	1.1789		1.200	
30	0.9680		1.0008	
60	0.8453		0.8589	
90	0.7853		0.7513	
120	0.7109		0.6674	
180	0.5444		0.5440	
210	0.5022		0.5022	
240	0.4703		0.4624	
270	0.4317		0.4294	
300	0.4068		0.4008	

It follows, therefore, from the experiments, the details of which are given above, that solutions containing both nitrous and nitric acids, whether prepared from silver

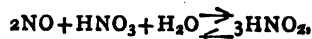
nitrite and hydrochloric acid, or from nitric oxide and nitric acid, or from nitrogen peroxide and water, or from nitrous fumes and water, have this one property in common, that the diminution of reducing material, presumably nitrous acid, therein contained, proceeds in accordance with the same law. The velocity of the change seems, however, to be dependent rather upon the ratio of nitrous to nitric acid than upon the actual masses of either of them. But though these solutions have this one point in common, yet in other respects they differ most markedly. For bubbles of gas, namely, nitric oxide, are rapidly given off from solutions prepared from nitrogen peroxide and nitrous fumes, and to a less degree from silver nitrite, though solutions from nitric oxide and nitric acid do not give off bubbles of gas in a similar manner. Again, all my former investigations (*Journ. Soc. Chem. Industry*, 1891, p. 1294) have shown that, whereas metallic lead does not readily dissolve in solutions containing nitrous acid and prepared from silver nitrite, yet it dissolves very rapidly in solutions equally containing nitrous acid, but prepared from nitrogen peroxide and water. The cause for the similarity on the one hand, and the dissimilarity on the other, must remain the subject of a fuller enquiry.

General Conclusions.

The main points of this enquiry may briefly be summarised as follows:—

(i.) The formation of the impurity of nitrogen peroxide in nitric acid, imparting to it the well-known yellow tint, takes place in the case of the more concentrated acid, even at a temperature of 30°, and of the less concentrated acids at from 100—150°, even when the acid is not unduly exposed to sunlight.

(ii.) The reaction between nitric oxide and nitric acid may be regarded as reversible, thus—



provided that the acid be sufficiently dilute, and the temperature sufficiently low. Under these conditions equilibrium is established between the masses of nitric acids when the ratio of the former to the latter is, roughly speaking, as 9:1. The actual ratio varies slightly on the one side or the other, according to the conditions of the experiments. With more concentrated acids and at higher temperatures the chemical changes taking place are more complicated and the decomposition of the acid more profound.

(iii.) The decomposition of solutions containing both nitric and nitrous acids is also investigated; the rate of the change is shown to be proportional to the mass of the nitrous acid undergoing change. The curve representing the amount of chemical decomposition in terms of the mass present is shown to be hyperbolic and illustrative of the law—

$$(I.) \frac{dC}{dT} = -\frac{C^2}{M}.$$

This holds good, whatever be the method employed for the production of the nitrous-nitric acid solution.

The observed values for C or the concentration of the nitrous acid are concordant with those calculated according to the above differential equation within the limits of experimental error.

The rate is dependent upon the ratio of the masses of the nitrous and nitric acid, being the more rapid the greater the proportion of the former to that of the latter.

In the particular case of the liquid prepared from nitric oxide and nitric acid, wherein the reproduction of solutions of similar concentration presents less difficulty, it is shown that, as the temperature increases in arithmetical the rate of change increases in geometrical proportion, in accordance with the equation—

$$(II.) v_t = v_1 k^{(t-t_1)},$$

the value for k being 0.0158,

Finally, though the nitrous-nitric acid solutions behave in a similar manner as regards the diminution of the mass of the nitrous acid, yet, in other respects, such as evolution of gases and the action upon metals, they are dissimilar.

In conclusion I would express my obligations to Mr. W. Esson for assistance in the mathematical portion of the paper, and to my colleagues for suggestions made in the course of the investigations.

ON THE GUNNING-KJELDAHL METHOD AND A MODIFICATION APPLICABLE IN THE PRESENCE OF NITRATES.*

By A. L. WINTON, Jun.

The Gunning Method (in Absence of Nitrates).

THE modification of the Kjeldahl method, proposed by Gunning in 1889, has since been indorsed by a number of well-known chemists.

The Gunning method is very simple, the only reagents used previous to the distillation with caustic soda being sulphuric acid and potassium sulphate, the latter taking the place of the three reagents—mercury (oxide or metallic), potassium permanganate, and potassium sulphide—ordinarily used.

The mixture of sulphuric acid and potassium sulphate boils at a high temperature, and, as a rule, oxidises the organic substance more rapidly than the ordinary mixture of sulphuric acid and oxide of mercury.

The results obtained by Gunning (*Fres. Zeit.*, xxviii., 188), Atterberg (*Chem. Zeitung*, xiv., 509), Van Slyke (*U.S. Dept. Agr. Div. Chem. Bull.*, xxxi., 142), and others, including the writer, on fodders, dairy products, fertilisers free from nitrates, and various organic substances, show that this method is fully as accurate as the ordinary Kjeldahl method, and, in some cases, gives better results. It is a well-known fact that the nitrogen of many alkaloids, azo-compounds, and various bodies of the aromatic series cannot be determined by the usual Kjeldahl method, but Gunning and Atterberg have obtained good results on morphine, quinine, indigo, and aniline oxalate by the Gunning modification.

The chief disadvantage of the method is the frothing which occurs during the first part of the heating. This frothing, however, causes but little trouble if a flask of at least 500 c.c. capacity (which can afterwards be used for the distillation) is employed and care be taken in adjusting the heat.

The Gunning mixture is, at ordinary temperatures, half solid, and must be heated before it can be measured for use. It is therefore best to add 18 grms. of potassium sulphate and 20 c.c. of sulphuric acid, separately and in the order named, to the flask containing the substance, shaking a few times before heating. The coarsely powdered sulphate may be conveniently measured out in a cartridge shell adjusted to hold 18 grms. and provided with a wire handle. The acid may be added from a graduated cylinder or a burette of wide calibre connected by a syphon with the acid reservoir ("Report Conn. Agl. Expt. Station," 1889, 192).

After the digestion is completed water should be added before the mixture becomes too cold, otherwise it is difficult to obtain a solution of the solid mass.

The writer has found that the fertiliser-chemical known in the trade as "high grade sulphate of potash," and costing but a few cents a pound, answers every purpose, and is, in fact, better than the white sulphate of the apothecary, being usually free from moisture and chlorides, the presence of which tends to increase the frothing.

Following is a comparison of results, obtained by the methods named, on those forms of organic nitrogenous matter which are most commonly used in mixed fertilisers and on four commercial fertilisers free from nitrates.

	Kjeldahl method.	Gunning-Kjeldahl method.
Cotton-seed meal	7'06	7'11
" "	7'10	7'13
" "	7'10	7'15
" "	6'95	6'97
Castor pomace	5'56	5'59
Tankage	5'03	5'07
"	5'72	5'82
Bone	4'03	4'02
"	3'92	3'90
Dry ground fish	8'69	8'77
" "	8'14	8'06
Peruvian guano	2'88	2'95
Mixed fertiliser*	3'45	3'45
" " †	3'00	3'00
" " ‡	3'80	3'76
" "	1'82	1'81

The Modified Method Applicable in the Presence of Nitrates.

In laboratories where fertiliser analyses are being made the adoption of the Gunning method would tend to complicate rather than to simplify matters so long as in the presence of nitrates nitrogen is determined by another method.

It is impracticable to add salicylic acid to Gunning's reagent, as such a mixture could only be used while hot, and it is important that the temperature be kept as low as possible during the early stages of the digestion. It occurred to the writer, however, that Scovell's mixture of sulphuric and salicylic acids might be used in the ordinary way, potassium sulphate being added later in the process in place of mercury. After a number of unsuccessful trials—unsuccessful because too much potassium sulphate was used and the boiling-point of the liquid became so high that oxides of nitrogen were driven off—the following plan was settled upon:—

The material, 0.5 to 1.0 grm., is digested with 80 c.c. of Scovell's salicylic acid mixture (30 c.c. of sulphuric acid and 2 grms. salicylic acid) in a flask of 600 c.c. capacity for two hours with frequent shaking. Two grms. of zinc dust are then slowly added, with continual shaking, and the flask heated, at first gently, until after a few minutes' boiling dense fumes are no longer given off. Thus far the process is the same as in the Scovell-Kjeldahl method (the official method of the Association of Official Agricultural Chemists), except that the digestion is continued for two hours, which, in some cases, the writer has found absolutely necessary in order to secure complete solution of the nitrate. Ten to twelve grms. of potassium sulphate are next added and the boiling continued for a little time after the solution is colourless or, if iron is present, has a light straw colour which remains unchanged. On cooling, as the mixture begins to solidify, water is added, at first slowly with shaking, and the distillation with caustic soda is carried on in the usual manner.

The trials thus far made with this method on nitrates and fertilisers containing nitrates have proved entirely satisfactory.

In the following Table are given the results obtained by the official method and the method here described, together with the percentage of nitrogen in nitrates as determined by the Schulze-Tiemann method.

The average of the twenty-five determinations by the Scovell-Jodlbauer method is 4.64 per cent, by the proposed method 4.65. The greatest discrepancy in any instance

* Contains 1.89 per cent nitrogen in ammonia salts.
† Contains 1.76 per cent nitrogen in ammonia salts.
‡ Contains 1.77 per cent nitrogen in ammonia salts.

is one-tenth per cent. In ten cases the proposed method gave the lower result, in thirteen cases the higher result.

	Nitrogen in nitrates by Schulze-Tie- mann.	Total nitrogen by Scovell-Jodlbauer.	Total nitrogen by proposed method.
Pure potassium nitrate	—	13'73	13'71
Commercial nitrate of soda	—	15'86	15'90
Tobacco dust	—	1'76	1'71
Mixture of ground bone, murlate of potash, and nitrate of soda	3'61	5'74	5'66
Mixture of bone, tankage, disc. bone- black, mur. potash, and nitrate of soda	1'46	3'81	3'85
Mixture of bone, tankage, dis. bone- black, sulph. and mur. potash, sulph. am., and nitrate of soda ..	0'63	4'15	4'07
Mixture of bone, tankage, dis. bone- black, sulph. and mur. potash, and nitrate of soda	0'43	4'03	4'10
Mixture of tankage, dis. bone-black, mur. potash, and nitrate of soda ..	2'23	4'41	4'51
Mixture of tankage, dis. bone-black, wood ashes, and nitrate of soda ..	1'63	3'85	3'85
Mixed fertiliser	0'56	3'82	3'86
"	2'39	6'89	6'99
"	0'69	4'84	4'89
"	1'55	3'45	3'47
"	0'36	3'05	3'10
"	0'86	2'70	2'65
"	1'54	3'56	3'63
"	0'21	2'84	2'79
"	0'83	3'69	3'76
"	0'12	2'83	2'77
"	0'95	4'84	4'91
"	0'70	2'48	2'44
"	0'68	2'56	2'56
"	0'38	3'56	3'55
"	0'91	2'54	2'58
"	2'91	5'02	4'96

THE ANALYSIS OF IRON AND STEEL.*

By JOHN PARRY, F.C.S., and J. JAS. MORGAN, F.C.S.

I.—INTRODUCTORY.

It requires only a moderate knowledge of chemical science to render one competent to carry out the general routine work of an iron and steel works laboratory. But it is of very great importance that the beginner should aim at becoming an expert and clean manipulator. Most of the methods of procedure hereafter described are very simple; yet the tyro will find that even the ordinary determination of carbon by the colour test cannot be done with anything like accuracy without considerable practice. And the same applies to the determination of the other elements—more especially phosphorus. All complicated and fragile apparatus are out of place, and fail to meet the needs of the iron and steel manufacturer, who requires tolerably accurate results, together with promptitude. The time consumed, together with the difficulty of keeping and maintaining delicate or elaborate instruments in perfect working order, and also the proportionately difficult manipulation, altogether forbid their use. The same may be said of the elaborate instructions given in an ordinary text-book on chemical analysis for weighing, drying, and transferring precipitates in their

entirety; they are useless in a practical iron works laboratory. In lieu of these operations, the steel works chemist simply folds up the wet filter paper containing the precipitate in the shape of a cone, and by gently blowing removes it from the funnel to the crucible, so that the base rests on the bottom, while the point is uppermost. He then places the crucible in the front part of the muffle until the combustion of the paper is complete, ignites immediately, withdraws, and cools quickly, generally by placing it on a thick iron plate, and covering with a glass shade. In nearly all steel works laboratories, directly ignition is complete, and the precipitate is sufficiently cool, it is thrown upon the pan. The counterpoising of crucibles is not practised, such operations being inadmissible through the time of his disposal being altogether inadequate. Were he to follow the routine generally described in text-books as regards the drying and burning of the filter paper and contents, the risk of error in his results would be considerably greater. As regards the employment of gas in the laboratory for igniting purposes, it certainly has many advantages, amongst them being that no risk from dust results from the use of the same as with a coke-fired muffle, a very great and important feature; while, again, its use may result in considerable economy. In a steel works laboratory, however, Bunsen burners for ignitions are too slow and altogether inadequate. A large muffle, heated by a coal fire, and through which a free draught of air circulates, should be employed. As regards weighing, most young chemists needlessly waste considerable time in this operation, forgetting that the results so obtained are covered by the experimental errors, which must occur in the course of chemical manipulation as practised under ordinary conditions. For practical purposes, it is useless to weigh nearer than one-half a milligram; while, in weighing large quantities, a limit of even a milligram may be allowed. It is of far more importance to become a clean and expert manipulator, to be able to pour out solutions to the last drop, as also to acquire the knack of transferring precipitates from one receptacle to another quickly and without loss, and to avoid the errors entailed by dirty apparatus. We have known instances in which these obvious sources of error have been quite ignored, the chemist consoling himself, when confronted with the discordant results so obtained, that these could not possibly be due to any fault of his, because he had always weighed the various portions of the sample taken for analysis, as also the resulting precipitates, with the greatest care, never allowing an error of one-hundredth of a milligram.

We have already stated that all complicated apparatus is altogether out of place in a steel works laboratory, which should be fitted up as simply as possible. The chief aim of the present day, however, seems to be to possess a laboratory which from an architectural point of view, leaves nothing to be desired either as regards design or fittings, but as far as the comforts of those who have to work in the same, or of its suitability as regards size and arrangement, is far from being perfect. In building a laboratory, the main object should be to obtain a large, well-ventilated and lighted room to serve as a general work room, with at least one good room fitted up for the reception of the balance, and also to serve as the library. This room should be made as dust-proof as possible, and in close proximity to the general work room or laboratory proper. The stove for heating the muffle should be so arranged that the firing is done in a room which would also serve as the store-room, while the muffle is in the balance room, and the top of the stove in the general room. The top of the stove should be formed with a hood and glass door to be used as a stench cupboard. In addition, the usual arrangements for gas burners should be fitted up in the laboratory at the convenience of the operator.

The methods, with the precautions to be observed, and given hereafter, are only applicable to the practical

* From *Industries*, August 30, 1889.

analysis of iron and steel, and as a rule only results of moderate accuracy are obtained. An exact scientific analysis either of iron or steel is altogether beyond the province of a practical steel worker; and for its successful application requires special scientific training to be obtained only in a laboratory devoted to physical and chemical research, under the tuition of a trained scientist. The main object of a works analysis is, as a rule, to keep the average chemical composition of the metal within certain known limits, so as to insure the production of a material, such as steel or iron, of average good quality, and free from any excess of injurious impurities; for it is quite impossible to always produce either pig iron or steel of exactly the same chemical composition. Unless, however systematic daily analyses are made, there can be no check on the manufacture, and in our experience the neglect of such analyses has always resulted in failure, attended with a serious pecuniary loss. We may remark also that the ordinary analyses of iron and steel, in which the silicon, carbon, sulphur, phosphorus, manganese, and sometimes copper and chromium, are determined, often fail to afford any explanation of the abnormal behaviour of certain samples when subjected to ordinary tests. So much is this the case, that many engineers and manufacturers are inclined to altogether ignore chemical analysis, and prefer relying solely on physical tests. While, on the other hand, others of equal repute advocate an extension, asserting that our ordinary analyses must be incomplete, and urging the chemist to search for some as yet unknown impurities, other than silicon, carbon, and sulphur, which may be present. A great deal of time and trouble has been expended on research of this class; but, on the whole, it may be said that the results so obtained have added very little to our present knowledge. It has been ascertained that both iron and steel always contain a notable proportion (by volume) of hydrogen and carbonic oxide gases, with smaller quantities of carbonic acid and nitrogen. It has not, however, been demonstrated that these gases affect the quality of the metal as such, or indeed whether they exist in combination with iron at all. They appear to only mechanically weaken iron, or more especially steel castings, by rendering them porous, the gases collecting in bubbles in the interior (causing what are technically termed "blow holes"), which consequently reduce the strength of the castings. Some chemists, however, assert that steel containing hydrogen is brittle; while others, on the contrary, hold that no difference can be traced between it and steel containing none. The same applies to nitrogen and carbonic oxide.

It has been shown that iron may contain, and indeed often does contain, other elements than those given in the ordinary analysis; but the enormous difficulty of absolutely quantitatively determining their presence, and freeing them from the great preponderating bulk of iron through which they are diffused, causes some to be sceptical as to the results given, to say nothing of the extreme care required to insure the complete isolation of the material undergoing analysis from external contamination, such as would accrue from the employment of impure chemicals, the doubt as to the absolute cleanliness of the apparatus, and last, but not least, the danger of contamination arising from the fact that the glass and porcelain vessels cannot be said to be absolutely insoluble in the strong acids and reagents used. Indeed, some of our best and most reliable chemists assert that it is impossible to avoid error from this latter cause, and that therefore all analysis should be performed in platinum vessels, and glass and porcelain be altogether discarded.

To avoid the manipulative difficulty of dealing with the immense masses of iron, as compared with the minute quantities of foreign ingredients presumably present, and the uncertainty of the complete separation of these by precipitation in the presence of an excess of metal, it has been proposed to reverse the usual process of endeavouring by precipitation to separate the impurities

from the iron, viz., to extract the foreign matter by digesting the mixed impure mass in suitable solvents. By this method copper, nickel, cobalt, magnesium, chromium, aluminium, calcium, and lead have been detected in steel by simply heating 10 ozs. of the metal with nitro-hydrochloric acid, evaporating nearly to dryness, digesting the pulpy mass with (1) water, (2) ammonia, (3) acetic acid, (4) sulphide of ammonium. The solutions are mixed together, evaporated to dryness with a small quantity of hydrochloric acid, re-dissolved, and upon subsequent examination are found to contain the above named elements, together with a small quantity of iron, which consequently renders analysis by the ordinary precipitation methods easy. This method has the further advantage that a quantity, utterly unmanageable when treated by the ordinary methods, may be taken for analysis; and further, that sensible quantities of the various impurities are obtained for weighing and examination. This work, however, up to the present has given little as regards results, and the quantities thus determined have, with a few exceptions, been found so minute as to lead many to doubt their efficacy either for good or evil.

It is probable that we have much to learn, and if we are satisfied that these bodies are contained in iron, it may, on the whole, be best to await further investigations. If, however, we admit that both iron and steel may contain minute proportions of these elements, it cannot be said that in the face of the fact—viz., that, as regards other metals, the introduction of a very minute proportion of some foreign ingredients is sometimes deleterious—these minute quantities can have no effect on iron and steel—we simply do not know. A well-known metallurgist has stated that the research for and determination of substances technically termed impurities of iron is nearly over, and that we have little left for research, except the so-called pure iron itself, which, after all, may be a compound body. Others assert that iron, in the form of an alloy, or in combination, is a very different material from iron as such. The study of the higher chemistry shows that it is probable that so-called "elements" are derived from one primary body; elements may be neither more nor less than equivalent quantities of this primary body. Crookes states that the rare earths such as didymium and yttrium, show a close mutual similarity in members of the same group; and yet, by his method of analysis, distinct differences have been tabulated, which the ordinary analytical methods failed to indicate. Should this be the case as regards so-called pure iron, it is evident that a wide field for further investigation is before us; and the fact that those who have made the study of iron their speciality are almost unanimously agreed that they have not seen, and have failed to manufacture, absolutely pure iron, renders it probable that it is so. Possibly, work done in this direction may afford a reasonable explanation of the fact which cannot now be longer ignored, viz., that physical tests often give results not at all corresponding to those inferred from the ordinary chemical analysis, and, indeed, these discrepancies have become so marked that it has been suggested that iron is possessed of some unknown property beyond the scope of analysis. This seems, in our opinion, a step in a backward direction, which, even with our present confessedly imperfect knowledge, cannot for a moment be allowed. We may be excused for saying that all this may have little or nothing to do with the metallurgical chemist of the future. It seems that the task before him is: (1) If iron be a compound body, to isolate and give the proportionate quantities of this problematic compound; (2) if iron undergoes, or partly undergoes, a molecular change, such as is well known to occur with other bodies, to isolate, as has been done with other substances, the iron molecularly changed, and of more importance still, to tell us whether iron is a body partly composed of iron as such, combined or intimately mixed with molecularly changed iron. It follows that for all practical purposes

it comes to the same thing to say that iron is a compound body, or that it has undergone a partial molecular change. The relative proportions of each must be isolated and weighed in the balance.

We know that in the case of metallic oxides, also of some of the metals and metalloids, under certain conditions they undergo allotropic change. In some instances a simple elevation of temperature suffices, and in the case of alloys Professor Roberts-Austen shows that modifications may be induced, rendering one portion of the alloy less soluble in acids than the other. (We would add here that the Cantor Lectures on Alloys, by Professor Roberts-Austen, are well worth reading, and convey a mass of information which should be studied by the practical metallurgist.) We may say that tin is capable of undergoing such an allotropic change: (1) a state in which it is hard and brittle, sp. gr. 6; (2) one which is malleable, sp. gr. 7.7; and many other instances might be quoted, and all quite familiar to the ordinary student. We repeat, that the analytical chemist must not, however, be content with mere words or formulæ when, say, a metal such as steel takes the form of, in one instance, a hard brittle substance, and in the other remains soft and malleable. It rests with him to determine by the balance whether these contrary effects are due to the introduction of foreign elements or, as before said, to molecular changes. In urging the chemist to investigate it must not be inferred that we indorse all that has been quoted on molecular change or difference; we can only say that such changes may occur, that further investigation is needed, and that a promising research is before him. Iron may exist in a more or less condensed state; in other words, its atomic weight may vary within certain narrow limits. Indeed, Crookes states that this is probable in the case of some of the elements. Another field for investigation, which may be termed practically feasible, arises from the results of a series of laborious microscopical studies of the fracture of various qualities of iron and steel, formulated by Dr. Sorby. (For the complete article on "Microscopical Structure of Iron and Steel," see *Journal of Iron and Steel Institute*, Part I., 1887.) Briefly, this operator has shown that iron and steel are not, as usually assumed, homogeneous, but rather heterogeneous bodies, which he classifies as follows:—(1) Free iron; (2) iron combined with carbon, an intensely hard compound; (3) pearly constituent compound of Nos. 1 and 2; (4) the pearly constituents, re-crystallised; (5) ruby-coloured crystals; (6) graphite; (7) slag; (8) slag and undetermined residue; (9) soluble metallic substances; (10) metallic substances less soluble; (11) schreibersite. It follows, therefore, if we accept Dr. Sorby's results in their entirety, that the elementary analysis of the metal, giving only graphite, combined carbon, sulphur, phosphorus, &c., can only furnish limited information, and should be supplemented, or even replaced by proximate analysis. The task before the chemist is to isolate these various compounds, and gravimetrically determine the percentage of each. It is now considered all but certain that neither iron nor steel is perfectly homogeneous; consequently many chemists have devised sundry methods for the separation of their constituents. Much, however, remains to be done, as a good all round method of proximate analysis has still to be devised.

(To be continued).

Nerve Tissues of Certain Invertebrate Animals.—Dr. A. B. Griffiths.—In the nervous tissues of insects and crustaceans, neurokeratine is replaced by neurochitine. The matter of the nerves of the lower animals is very unstable. When fresh it is slightly alkaline, but becomes acid shortly after death.—*Comptes Rendus*, cxv., No. 16.

ON IRON RUST POSSESSING MAGNETIC PROPERTIES.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

My attention was first drawn to this matter in January, 1889, when walking along the pier at Clifton Springs, Port Arlington, Victoria, by noticing the large scales of rust attached to the old tram rails, which had not been in use for some years. On breaking off fragments I was much struck by their resemblance to the crust seen on many metallic meteorites. Some of the pieces were from a quarter to one-third of an inch through, one to two inches wide, and three to four inches long. Although retaining somewhat the form of the original iron they were very brittle, and, on breaking them across, the fracture had a slight resemblance to that seen in some non-crystalline magnetites. Further, on scraping the rust and breaking pieces off with a pocket-knife, the dust and fragments were strongly attracted to the blade which had been magnetised. I could see no traces of metallic iron, and felt sure that practically there were no particles of the metal in the rust. I could not, of course, make quite certain without other appliances, so on my return to Sydney I examined the rust carefully for metallic iron by grinding it in an agate mortar, but could not find the smallest speck of metal; the material ground readily to the last portion and yielded a dark brown coloured powder, and, to my surprise, I found the powder to be wholly attracted by the magnet, and not merely in part as I expected. I did not care to publish the above as it rested upon observations made upon a single specimen, and was directly opposed to the usual statements in text-books and works of reference on chemistry, that rust is a non-magnetic hydrated sesquioxide of iron, and an opportunity to proceed with the matter did not occur until September last.

It may be thought that more has been made of the matter than its comparative unimportance warrants, but as my results are at variance with the general statements placed before students and others (statements which are of many years' standing), it is perhaps not unjustifiable to place sufficient evidence on record to establish the facts and place them on a firm footing. Fortunately the statements can be verified by anyone possessing a magnet, no matter how poor a one it may be, inasmuch as material can be obtained from any old piece of rusty iron.

Since then I have been able to examine other specimens of rust and to make a few experiments upon the matter, all of which bear out the original observation and show that ordinary iron rust is usually attracted by the magnet.

By magnetic rust or oxide in this paper is meant iron oxides, which are attracted and lifted by a small bar magnet of one-eighth of an inch in diameter, or by an ordinary penknife blade which had been magnetised; but when seeking to separate large quantities, a bar magnet which would lift four ounces of iron or an electro-magnet lifting eighteen ounces was employed. As mentioned in a preceding paper, a powerful electro-magnet was considered inadmissible.

In spite of all the care exercised in grinding and using the magnet under water, there may still be some non-magnetic oxide mechanically enclosed and carried over by the magnetic particles, as is seen when it is attempted to separate sulphur and iron filings by a magnet; but from the number of times that the same powder can be lifted without leaving anything behind I think it cannot amount to much, and may be neglected as unimportant.

The source of the iron rust and the conditions under which it had been found are given in what might appear

* From the *Transactions of the Australasian Association for the Advancement of Science*, Hobart Meeting, 1892.

as unnecessary detail, but full particulars are furnished so that it may be seen that iron of various qualities, e.g., common, cast, inferior, and the best malleable iron and steel all furnish rust containing magnetic oxide in the early stages of the rusting, and that under certain circumstances the final products—the sesquioxide and hydrated sesquioxide of iron—may also be magnetic.

Metallic iron was tested for in every case by careful examination for specks of metal when grinding in the agate mortar, and also by digesting the powder in a solution of iodine in potassium iodide for some hours, but proved to be absent except in one or two cases, which are mentioned further on.

No. 1.—Rust from Iron Rails: Clifton Springs, Port Arlington, Victoria.

This specimen was collected, as stated above, in January, 1889, from the old tramway on the pier at Clifton Springs, Port Arlington, Victoria.

9·1 grms. were crushed and sent through a No. 60 sieve. The dark brown powder was wholly attracted by the magnet, the amount of non-magnetic powder left after repeated applications of the magnet being almost invisible. The attempted separation of any non-magnetic matter was repeated time after time, so as to get rid of any entangled non-magnetic dust, but always with the same result.

The rust was also acted upon by the magnet under water, after re-crushing to an impalpable powder in an agate mortar. This was done to avoid as far as possible non-magnetic oxide being lifted mechanically between or by attached particles of magnetic oxide; but after many repeated attempts to obtain non-magnetic rust from it, I had to come to the conclusion that it was all attracted by the magnet.

Another attempted separation was made on 5·640 grms. powdered in an agate mortar, but with a like result, i.e., the whole was attracted.

These scales of rust were found to be not only magnetic, but some were also polar, i.e., they not only attracted one end of the magnetic needle but also repelled the other, and the opposite edges of the fragments possessed opposite polarities; moreover, when suspended in a stirrup by unspun silk some specimens set themselves in the magnetic meridian, a further proof of their being magnetic and not merely lumps of ordinary rust containing particles of metallic iron.

The specific gravity was found, by Joly's apparatus, to be 4·07 at 18°, native magnetite being 4·9 to 5·2.

A portion of this rust yielded 70·11 per cent metallic iron (by the bichromate volumetric process), the theoretical amount in magnetic oxide, Fe_3O_4 , being 72·41 per cent.

To confirm, or otherwise, the results obtained from the old rail, rust specimens were collected from various sources, and these on examination verified the previous observations in almost every particular.

The rust in each case was scraped off with a horn spatula and crushed in a porcelain mortar, and the precautions taken were such as to prevent any metallic iron finding its way in; further, the magnetic powder was in every instance proved to be free from any particles of iron.

No. 2.—Rust from an Old Iron Waggon lying on Lady Robinson's Beach, near Sydney.

The scales are about one-eighth of an inch thick, and come off in large flakes five or six inches across. On the outside, as well as the inside (i.e., next to the still unoxidised iron of the waggon), they present the usual appearance of rust, being scaly, and of a dark brown colour with light ochrey patches, with here and there a small cone-like excrescence. Specific gravity at 16° C. = 3·76.

On breaking the scales across they present a dark—

almost black—coloured interior with a well marked fibrous crystalline structure, such as is seen in many Goethites. This internal part gives a dark brown streak or powder, the outer film gives a pale ochre-coloured powder. The rust is picked up bodily by a magnet—whether a magnetised knife-blade, a horse-shoe, or electro-magnet is used—and some of the scales show well-marked north and south poles. On being crushed it yielded a dark brown powder, which was found to be wholly lifted or attracted by a magnet, i.e., no non-magnetic portion could be obtained from it.

In one case 409 grms. were crushed and sent through a No. 30 sieve; only one grm. was left by the magnet, and this was seen to consist of rounded grains of sand from the beach.

Another portion was crushed and sent through a No. 60 sieve; this likewise was wholly attracted by the magnet.

A third portion was scraped on both surfaces before crushing. The outer crust or scrapings—5·25 grms.—gave a yellowish brown-coloured powder, which was wholly lifted by the magnet; the inner dark and crystalline part, weighing 432 grms., gave a brown powder, and was also entirely magnetic.

Cakes of this and other rusts, $\frac{1}{16}$ to $\frac{1}{4}$ ths of an inch, and of three or four inches superficial area, are drawn to a horse-shoe magnet capable of sustaining a pound weight of iron, with a slight jump like pieces of thin sheet-iron, but with, as might be expected, very much less readiness.

No. 3.—Rust from an Old Wrought-Iron 400-gallon Water-Tank, made of thin "boiler" plate, and used for shipping malt to Sydney.

Specific gravity = 3·90 at 18° C. This had the usual appearance of rust scales, but was strongly magnetic. Distinct north and south poles were shown by some of the large pieces; 13·3 grms. were crushed and sent through a No. 60 sieve; the brown powder was wholly lifted by the magnet. A second sample, weighing 10·545 grms., was also found to be wholly magnetic.

Another fragment or scale was crushed in an agate mortar, and 10·205 grms. of an impalpable brown powder obtained. This was placed in a glass spitz-kasten (or Knop's soil-washing apparatus), and separated into three portions of different specific gravities, but all were found to be attracted by the magnet.

The yellow ochre-like superficial rust from some of these scales, 8·096 grms. in weight, was ground to an impalpable powder and dried in a water-oven; and even this was wholly attracted by the magnet, although feebly.

No. 4.—Rust from an Old Flue Pipe, but which had never been used.

Some of this was powdered and sent through a No. 60 sieve; the light brown coloured powder yielded 2·25 of strongly magnetic and 2·3 grms. of feebly magnetic powder.

No. 5.—Rusts from Old Bolts, Bars, &c., which had been lying exposed to the weather in a wooden box.

Of the usual "rust colour" and appearance. The powder yielded—Magnetic particles, 7·71 grms.; non-magnetic particles, 0·205 grm.

No. 6.—Rust from Old Wrought-Iron Tyre.

Weight of powder = 4·691 grms. In separating this under water a certain amount of fine powder was obtained in suspension, and this apparently was not attracted; at any rate it could not readily be removed from the water by the magnet, but on evaporating it down on a sand bath it was found to be wholly lifted by the magnet.

Another specimen of the same, weighing 9·856 grms., was crushed in an agate mortar, dried in water-oven, and also found to be wholly lifted by the magnet.

No. 7.—*Rust from Old Sheet-Iron Barrow*, probably formerly galvanised.

The scales showed well-defined north and south poles. 146 grms. were crushed and passed through a No. 30 sieve. The whole of the dark brown powder was found to be attracted by the magnet.

No. 8.—*Rust from Old Disused Boiler-Plate Chimney*.

60 grms. were crushed and passed through a No. 30 sieve and yielded a dark brown powder, the whole of which was magnetic. The scales were also polar.

This example is not of so much value as the others, because it might be thought that the scale consisted of or contained magnetic oxide (Fe_3O_4), which had been formed at a high temperature, although personally I am satisfied that it was formed by the ordinary process of atmospheric rusting.

No. 9.—*Rust from Old Tinned-Iron Can*.

All traces of metallic tin had disappeared. 1.6 grms. were crushed and passed through a No. 60 sieve; the light brown powder was wholly lifted by the magnet.

No. 10.—*Rust from Scrap Heap*.

In the form of cakes, from $\frac{1}{4}$ th to $\frac{1}{2}$ th of an inch in thickness, and of several inches superficial area. The cakes were of the usual dark brown colour, but with soft powdery yellow-ochrey patches and cones or excrescences. These were detached and ground separately in an agate mortar, and found to be nearly free from magnetic particles, but the soft black powder found under the excrescences or pimples was highly magnetic.

No. 11.—*Rust from Flat Iron Bars*.

These had been left lying on the ground exposed to the weather; the whole of the rust was highly magnetic.

(To be continued.)

NOTICES OF BOOKS.

Chemical Lecture Experiments. Non-Metallic Elements.

By G. S. NEWTH, F.I.C., Chemical Lecture Demonstrator in the Royal College of Science, South Kensington. London and New York: Longmans, Green, and Co. 1892. 8vo., pp. 324.

THE aim of this work, as we are told in the preface, is twofold. It is to supply chemical lecturers and teachers with a selection of experiments suitable for illustrating the preparation and the properties of the non-metallic substances. Secondly, it is to serve the student as a companion to the lecture-room, giving the details of the experiments which he is likely to see performed, and saving him the trouble of taking notes and of sketching apparatus. It will be at once evident that the experiments are well selected and fully and clearly described. The illustrations scarcely leave anything to be desired.

Critical and dangerous experiments have been intentionally omitted. Like those which show the action of substances upon animal life, they are best committed not to the student but to the "researcher,"—if so questionable a word may be used.

Mr. Newth tells us that whilst adopting the metrical system, he has added the English equivalents of the French measures of length. The sole reason why the metric system of weights and measures has not long before this become dominant in England is its nomenclature, utterly repugnant to the genius of our language.

An interesting experiment has been devised to show the part played by suspended matter in that unhappy task the formation of fog. Mr. Newth's work is admirably adapted for students attending courses of lectures on inorganic chemistry.

A Short Manual of Analytical Chemistry, Qualitative and Quantitative, Inorganic and Organic. Arranged on the principle of the Course of Instruction given at the South London School of Pharmacy. By JOHN MUTER, M.A., Ph.D., F.R.S.E., F.I.C., F.C.S., &c. Fifth Edition, Illustrated. London: Messrs. Simpkin, Marshall, and Co., Ltd., and Messrs. Baillière, Tindall, and Cox. 8vo., pp. 212.

THIS manual, which may boast of having now reached its fifth edition, is fully worthy of the reputation which it has earned. Dr. Muter, much to his credit, tells us that his treatise is not intended to be a mere "examination book." It differs from the general run of the ordinary analytical manuals in including a number of the most important organic substances, instructions for the analysis of water, foods, and drugs, for colorimetry, and for the application of the polariscope and the spectro-scope. On the other hand, we must admit that some of the elements—those chiefly of little interest in pharmacy—have been excluded.

The chapter on the detection of alkaloids and on toxicological procedures is very ably written. Its chief defect is the omission of two very formidable poisons, aconitine and atropine. For this defect, however, Dr. Muter is not to blame. These substances, as he reminds the reader, can only be certainly detected by experiments on animals,—a method which is not only "a grievous sin," but illegal, save under a special licence not always to be obtained. In fact, to many toxicologists it would be easier to run over to Calais and to perform the experiments there.

Gas-analysis is here rather briefly noticed, but the student is referred for all necessary details to Sutton's well-known "Volumetric Analysis." We have no doubt that the present edition of Dr. Muter's work will still enjoy the favour which competent authorities have awarded to its predecessors.

Everybody's Writing-Desk Book. By CHARLES NISBET and DON LEMON. London: Saxon and Co.

WE have here a very curious, but we must at once admit, an exceedingly useful book. The introduction contains a most valuable suggestion:—"It is a good rule, so far as practicable, to watch the times and the seasons, and take pen in hand only when the subject is in the ascendant." But the man of Science generally labours under the disadvantage that none of his subjects is in the ascendant.

Contrasting work which is slowly and patiently elaborated with that which is a spontaneous outburst, the authors evidently seem to award the palm to the latter; but in some subjects such rapid utterances are out of the question. A writer like Darwin, busy up to the last moment in weighing the results of new experiments, new observations, and new criticisms, cannot dash off his theories as the poet, the divine, or the novelist may pour forth his master-pieces.

The authors call attention to the following points as to be observed in writing: (1) arrangement; (2) compass; (3) words and their mutual congruity. Few, we fear, after seeing how these points are here worked out will fail to see that they have been not unfequent transgressors in these important respects. But there is one class of defects in modern writings which Messrs. Nisbet and Lemon seem to have overlooked. We find no protest against the use of words taken in an illegitimate meaning, vulgarisms, slang expressions, and Americanisms. It is distressing to find "phenomenon" used to signify something unheard of; yet this error, originally confined to the advertisements of strolling actors, has become epidemic and has even attacked the medical papers. Among Americanisms the authors would have done well to denounce the verbs "to donate" and "to loan"—expressions as needless as inelegant, yet unfortunately "going the round of the papers."

The section on "synonyms and antonyms" will prove exceedingly useful. A writer, whilst possessing perfectly clear ideas, may often have to pause for the most suitable manner of expression. Here the "Writing-Desk Book" will often come to his aid. We must, however, beg to protest against "fragile" and "weak" being accepted as synonyms for delicate. If a person in bad health is spoken of as "delicate," one who is perfectly sound may be pronounced "indelicate." Of this a remarkable case is on record. A lady, speaking of her nephew, said "when he was little we all feared he would be very delicate, but now he has got into his teens he is as indelicate as a boy as you could find in a day's journey."

A few vulgarisms have found their way among the synonyms. "Gabby" is surely not to be recommended as a synonym for talkative.

Science Instruments. Catalogue of Scientific Apparatus and Reagents. Manufactured and Sold by Brady and Martin, Northumberland Road, Newcastle-upon-Tyne, and at 29, Mosley Street. 1892.

We are sometimes told that our predecessors, Scheele, Davy, Wollaston, and others, obtained admirable results without that plethora of appliances which figure in modern catalogues. With gallipots and saucers, crucibles and tobacco-pipes, they made capital discoveries. Hence it is asked why cannot we do the same? In reply to this insinuation we remind the objectors that it was just the same with gold-digging in the early days of Australia and California. With a spade and a pickaxe, a dish and a bucket, the digger brought to light grains and nuggets in abundance. But this state of things has come to an end. The alluvial deposits are exhausted, and they who would now obtain gold must be prepared to grapple with quartz-reef, and bring to bear chemical and mechanical skill backed up with no inconsiderable capital before they can secure the precious metal.

In chemical research the case is precisely the same. The facts and the conclusions which lay near the surface have already been made known, and to effect any advance in Science we must have at command instruments of precision such as we find figured and described in the excellent catalogue before us. Here we see a full and judicious assortment of apparatus to meet the requirements of the student, the analyst, and the man engaged in original research. Whether as a nation we are really advancing in experimental Science is, perhaps, not absolutely certain, but the demand for apparatus, chemical and physical, is largely on the increase. It is also plain that the instruments offered are improving in quality.

Apparatus for gas-analysis figures more and more largely in the catalogue of dealers, as it is well shown in the list before us. Filter-pumps also are becoming more and more appreciated. Bacteriological apparatus, so imperatively needed in sanitary analysis, figures here largely and includes the most improved instruments.

In the list of microscopes we notice what is apparently a curious typographical error. Under Beck's laboratory microscope (No. 754) we notice that it is fitted with an "Irish diaphragm." This, we presume, should have been "Iris diaphragm."

Physical and meteorological appliances are also not omitted. Three different spectrosopes are figured. Even anthropometric apparatus is here given, the writers pointing out the grave importance of such measurements and registrations.

The catalogue of reagents and chemicals presents a novelty which seems to us very useful. Many of the rarer chemicals are not quoted, but we are informed in a note that they can be supplied on application. This catalogue will be found very useful to the chemist and the student by aiding them in the selection of apparatus which they may require for any purpose. The prices quoted are decidedly reasonable for accurate, trustworthy instruments, and for pure reagents.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 16, October 17, 1892.

Reaction alleged as Peculiar to Spermine.—M. Duclaux.—If spermine possesses energetic curative properties, the properties are absolutely independent of its action upon magnesium in presence of platinum or copper chlorides.

Novel Preparation of Acetylene.—L. Maquenne.—The author decomposes crude barium carbide by cold water, which is added drop by drop so as to avoid a too sudden heating of the mass. The acetylene is given off regularly at a speed proportional to that of the afflux of the water, and it may be at once passed into the apparatus in which it is to be used. One hundred grms. of the barium carbide give from 5200 to 5400 c.c. of gas containing from 97 to 98 per cent of acetylene, and 2 to 3 per cent of hydrogen, with an appreciable admixture of any other hydrocarbon. If this gas is slowly passed through a long glass tube at a dull red heat it yields in the course of a day several grms. of synthetic benzene.

Analysis of Mixtures of Ammonia and of Methylamines.—H. Quantin.—This paper will be inserted in full.

MISCELLANEOUS.

Sewage Pollution.—The town of Bury (Lancashire) has been fined £20 for polluting the river Irwell. The daily output of sewage at Bury has amounted to one million gallons. Further offences will be more strictly dealt with.

Index to the Literature of Explosives.—The manuscript of Part II. of the "Index to the Literature of Explosives," by Charles E. Munroe, Torpedo Station, Newport, Rhode Island, U.S.A., is now ready for printing, and, provided a sufficient number of subscriptions are obtained in advance to warrant doing so, it will be issued in pamphlet form, of approximately 150 octavo pages, at 100 dollar per copy. Part I., issued in 1886, contains the titles of all articles relating in any way to explosives that appear in—

American Journal of Arts and Science ..	1819—1886.
Philosophical Transactions of Royal Society ..	1665—1882.
Journal of Royal United Service Institution ..	1857—1885.
Proceedings U.S. Naval Institute	1874—1885.
Revue D'Artillerie	1871—1884.
H.M. Inspectors of Explosives Reports ..	1873—1885.

Part II. continues the index for the above periodicals up to 1891, and contains the following in addition:—

Dingler's Polytechnisches Journal	1820—1890.
Proceedings American Chemical Society ..	1879—1890.
Nicholson's Journal	1797—1813.
Popular Science Monthly	1872—1890.
Edinburgh Journal of Science	1824—1832.
Brande's Journal of Science	1816—1830.

This index has been made by a careful search of each page of each of the 984 volumes included in it, and is believed to be complete from the date of first issue of each of the periodicals named.

New Process of Producing Caustic Soda, &c., from Brine by Electricity.—The *North-Eastern Daily Gazette* (Middlesbrough) announces a new discovery which it regards as potentially "second only in importance to

the North of England to John Vaughan's famous opening up of the Cleveland ironstone." It is the discovery of a new and simple process of producing caustic soda, chlorine, and other chemical products direct from the brine by electricity. The most careful tests applied up to the present time show, says the *Gazette*, an economy of over 50 per cent as compared with present methods. It is described as the simplest of all the known processes of soda making, the caustic soda being produced direct from the brine in one operation instead of two. At present carbonate of soda is first produced, and from that the caustic soda is made. "The valuable chlorine is also saved and utilised for the production of bleaching-powder and other by-products." Eminent chemists and electricians have already pronounced the new method a complete success from a chemical point of view, and it is said that there is every prospect of its being worked as a commercial success. Our contemporary regards it as of the greatest promise for the future of the North of England, which is at present too much dependent on the iron trade alone.

MEETINGS FOR THE WEEK.

MONDAY, NOV. 7.—Royal Institution, 5. General Monthly Meeting.

FRIDAY, NOV. 11.—Physical Society, 8. Continued discussion of the papers by Mr. Williams and Mr. Sutherland, "Dimensions of Physical Quantities" and "Molecular Forces."

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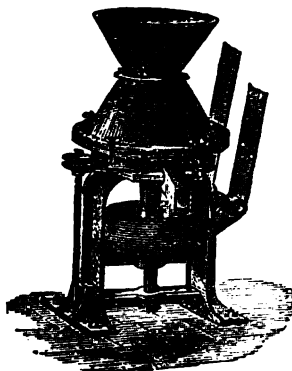
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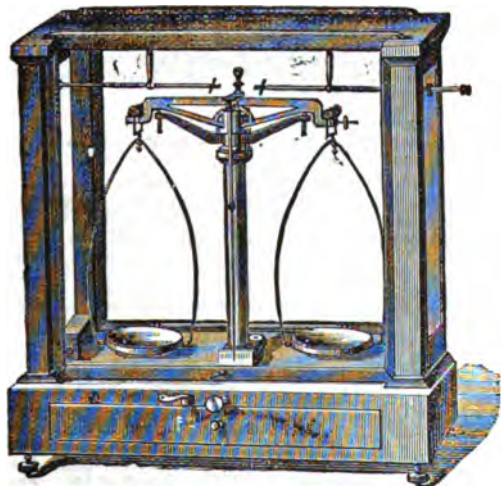


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THE CHEMICAL NEWS.

VOL. LXVI., No. 1720.

VOLATILE FATTY ACIDS OF BUTTER.

NOTE ON A RECENT PAPER BY WILLIAM JOHNSTONE.

By H. DROOP RICHMOND.

In the *CHEMICAL NEWS*, vol. lxi., p. 188, appears a paper entitled "Volatile Fatty Acids of Butter," in which the author draws the conclusion that "the solid fatty acids which collect in the condenser (during a Reichert-Wollny distillation) consists (*sic*) of—

18.6 per cent of pseudo-oleic acid,
81.4 " " myristic acid."

In a previous paper (*Analyst*, xvi., 26) he had shown that they were mainly capric acid, a conclusion which he has to all appearances abandoned.

There is in the paper strong internal evidence that his conclusion is unwarranted. After following the method I have previously found necessary with papers by this author, and correcting the mistakes in simple arithmetic, and translating his language into readable English, I find his procedure to have been as follows:—

He distilled the solution obtained by treating 5.433 grms. of butter-fat (probably not butter) according to Wollny's directions, and presumably collected 110 c.c. of distillate; at this stage he obtained 0.273 grm. of fatty acid by presumably washing out the condenser tube, and washing and drying the fatty acids therein. This quantity was used up for a determination of the iodine absorption, the figure found being 16.74 per cent iodine absorbed.

Water was then added and the distillation proceeded with until the flask (or retort) broke; the quantity of fatty acids obtained was 0.332 grm., and more would probably have passed over had not the accident occurred.

The total quantity collected was, then, $0.273 + 0.332 = 0.605$ grm., or 11.14 per cent (not 0.506 grm., or 9.31 per cent). The second fraction of 0.332 grm. was converted into a barium salt, of which 0.355 grm. (if the weight of the salt dried at 100° is assumed to represent the weight of the dry barium salt, or 0.354 if that dried at 130° is so taken) was taken and gave 0.136 grm. of barium sulphate by ignition with sulphuric acid; the barium salt is then equivalent to 0.276 (or 0.275) grm. of fatty acid; as the author evidently takes the weight of the salt dried at 100° to represent the weight of the dry salt, I follow him. Out of his total of 0.605 grm. of fatty acids collected, he has used 0.273 to determine the iodine absorption, and 0.276 to determine the barium in the barium salt; this leaves only 0.056 grm. for further examination, even if we admit that nothing was lost in the various operations.

He then took a further portion of his acid (of which only 0.056 grm. were available), converted it into a lead salt, washed it with alcohol, and thoroughly extracted with ether; he decomposed his lead salt, took the melting-point of the fatty acid thus obtained, dissolved it in alcohol, and converted it into an ammonium salt; from this he prepared a silver salt. Assuming that nothing was lost in manipulation and that only 20 per cent was soluble in ether (a low figure, seeing that the extraction was thorough), the total possible quantity left could not exceed 0.045. He, however, finds 0.456 grm. of silver salt, which contain 0.1465 grm. silver, and are therefore equivalent to 0.311 grm. of fatty acid; this fatty acid he shows to be myristic acid by a silver determination in the silver salt and the melting-point.

He has therefore succeeded in synthesising 0.266 grm. of myristic acid; there is strong evidence that it is syn-

thetic on account of the extreme purity of the acid, shown by the agreement of the melting-point found, 53.2° , with that given by Krafft, 53.8° , for the pure acid; had the acid been naturally existing and separated by the procedure he followed, it would not have been nearly as pure.

By means of a little juggling with figures and formulæ he is enabled to conclude from a determination of the iodine absorption on one fraction, and a determination of the properties of a substance evolved during the treatment of a second fraction, that the solid fatty acids collected consist of—

18.6 per cent of pseudo-oleic acid,
81.4 " " myristic acid.

He gives no clue as to how he identified "pseudo-oleic" acid, a substance whose properties are not yet generally known; he does not say whether it is the same compound previously described by him (*loc. cit.*) as "iso-oleic" acid. The publication of his researches on this compound will be interesting.

His conclusion must be considered as, to say the least, unwarranted by his experiments.

He presumably distilled further quantities of this butter-fat in the same manner, and examined the soluble volatile acid; he now finds notable quantities of acids of molecular weight higher than butyric acid in the distillate, while in the paper cited he found only butyric acid, and in a former paper (*Analyst*, xiv., 113) he mentioned propionic, acetic, and formic acids. There is hope, then, that in a few years he may find the same results as other observers.

50, Clanricarde Gardens, Bayswater, W.,
October 22, 1892.

ON THE LIQUEFACTION OF GASES BY ELECTRICITY.

By H. N. WARREN, Research Analyst.

THE usual method employed for rendering a gaseous body liquid, such, for instance, as chlorine, sulphur dioxide, &c., is as well known, prepared either by the action its own pressure exerts when evolved in a confined space, or by artificially lowering the temperature of the same, or thirdly, by a combination of both.

A brief description of the electrolytic method will, therefore, suffice to explain the strong analogy that exists with respect to both methods, save that at present the latter method is better adapted when a compound gas is desired, such, for instance, as HCl, &c. The apparatus employed consists solely of a stout glass combustion-tube, bent at right angles, and closed at either extremity, the longer limb containing two small platinum plates fused into the extremity of the tube, the bend of the tube containing a small plug of asbestos, soaked or saturated with strong H_2SO_4 for the purpose of retaining moisture. For the preparation of liquid HCl a sufficiency of a strong solution of HCl is introduced covering the platinum plates, and the asbestos plug inserted in the bend of the tube. The other extremity, being accurately sealed, is introduced into a freezing mixture of ice and salt.

To the outer extremity of the platinum plates, which should for convenience sake terminate in the form of wire, is connected a voltaic battery capable of quickly decomposing the acid. Large volumes of hydrogen gas, together with chlorine, are at once evolved, and becoming confined in the smaller end of the tube, aided by the low temperature produced by means of the freezing mixture, the gaseous HCl rapidly assumes the liquid form, the liquid thus produced being of a deep yellow colour, and often crystallises, due to the excess of chlorine present. If now the tube and its contents are withdrawn from the freezing mixture and the circuit discontinued,

the liquid gas is quickly reabsorbed by the water, forming a highly chlorinated solution, which experiment may be again performed as before; a number of other similar gases may be also thus liquefied.

An interesting reaction is also afforded when acidified water is substituted in place of the HCl solution, the condensing part of the apparatus being also provided with a very thin platinum plate, to the surface of which is attached some platinum black. On re-connection with the batteries, the usual decomposition of the water takes place, and the partially liberated gases, owing to the intense pressure they are exposed to, together with the surface action afforded by the presence of the finely-divided platinum, explode at intervals, each time generating small quantities of water, which was found on examination to contain large quantities of H_2O_2 , besides retaining most obstinately the powerful odour of ozone.

The above reaction may be made altogether more striking, and affords an excellent lecture experiment, by employing a small quantity of water containing a few drops of chromic acid, to which a sufficiency of ether has been introduced, and intended to form a layer upon the surface; the ether quickly assuming a deep blue colour, due to its absorption of the well-known blue oxide of chromium. By substitution of the acidified water, various other compounds, such, for instance, as acetylene, may be readily formed. For the liquefaction of oxygen and hydrogen gas, a modified condensing arrangement is being constructed, and the author hopes before long to be able to communicate to these pages explicit details concerning the same.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

NEW METHODS FOR QUANTITATIVE ANALYSIS.*

By A. BAUMANN.

(Continued from p. 225).

PFLÜGER, like Kjeldahl, calls attention to the fact that in very dilute solutions the free acid liberates an equivalent quantity of iodine with extreme slowness. The liquid mixed with solution of thiosulphate until the iodine colour disappears is coloured yellow again by the separation of iodine. The process lasts for many hours, and seems to come to no conclusion. Hereby larger quantities of iodine are liberated than that equivalent to the acid to be determined. Hence the supposition upon which the method is founded is inaccurate, as there is no certain indication when the action is completed, and the liberation of iodine is occasioned by other causes.

The experiments of Pflüger prove indeed that mixtures of potassium iodides and iodates permanently decompose each other by liberation of iodine, but this decomposition is so slight that for twenty-four hours it may be put = 0. Pflüger has removed the evil that the titration in very dilute solutions takes longer time by using a sufficient excess of iodide and iodate. If about 5 c.c. of sulphuric acid (1 c.c. = 0.001 gm. N) have to be determined in a dilution of about 500 c.c., the titration is completed in about a quarter of an hour, if the liquid to be titrated is mixed with 10 c.c. of a 20 per cent solution of potassium iodide and 13 c.c. of a 4 per cent solution of iodate. The quantity of solution of thiosulphate consumed in a quarter to half an hour indicates exactly the quantity of iodine equivalent to the free acid, so that even at an extraordinary dilution perfectly useful results may be obtained under the above-mentioned conditions. These directions, however, are valid only if ammonium salts are absent.

Continually occurring separation of iodine is consider-

ably increased in dilute solutions by the presence of ammonium salts, especially if iodine salts are present in larger quantities. The explanation of this circumstance must be sought in the fact that in presence of ammonium salts ammonium iodide and iodate are formed, and that in a solution of both these salts a continual separation of iodine occurs, which is especially energetic in concentrated solutions. Pflüger has ascertained the conditions which must be observed if ammonia or free sulphuric acid has to be determined in presence of ammoniacal salts.

According to the author's experiments the titration is completed in about one hour if about 1 to 10 c.c. of sulphuric acid is present in excess (1 c.c. = 0.001 gm. N), if it has to be determined in about 450 c.c. of liquid, and not more than 1 c.c. of a 20 per cent solution of potassium iodide and 13 c.c. of a 4 per cent solution of potassium iodate are used. The quantity of the ammonium sulphate present may correspond to as much as 50 m.grms. nitrogen. If the total volume of the liquid to be titrated amounts to less than 450 c.c., the end of the titration is reached more rapidly, and after the lapse of an hour the true value will have been exceeded. If the utmost accuracy is required, it is well to make up the liquid always to the same volume, i.e., to 450 c.c.

If the titration is to be executed more rapidly, we add 2 c.c. of solution of potassium iodide and 2.6 c.c. of solution of potassium iodate to 450 c.c. of the liquid to be titrated. The true value is then found in a quarter of an hour.

In order to bring the process at once to a conclusion we take to 450 c.c. of liquid, 3 c.c. potassium iodide and 3.9 c.c. potassium iodate. A larger quantity of the iodine salts should not be used.

Pflüger prefers in general to use minimum quantities of iodine salts, as he has no experience to decide whether in an expedited titration slight differences in the temperature of the laboratory may not occasion greater differences.

Gröger recommends the iodometric method for the determination of acids and bases. He uses a decinormal solution of thiosulphate, a decinormal sulphuric acid, and perfectly neutral solutions of potassium iodide and iodate. The solutions of potassium iodide (24 grms. in 100 c.c.) and iodate (4 grms. in 100 c.c.), are kept separate and before each experiment equal volumes of both solutions are mixed in the quantities required.

In order to ascertain the efficient value of the solution of thiosulphate, Gröger weighs about 0.15 gm. of pure, dry potassium iodate with accuracy, dissolves it in little water, and adds about six times the quantity of potassium iodide. The iodine is liberated by an excess of hydrochloric acid, and the solution of thiosulphate is run in until the liquid is totally decolourised, using starch-paste as indicator. The standard of the decinormal acid is ascertained in the ordinary manner.

In determining free alkalies we supersaturate with a known quantity of decinormal acid and determine the excess of the latter iodometrically, with the addition of 5 c.c. of the solution of potassium iodide and iodate. In this manner Gröger determined most successfully both known quantities of potassa and soda-lye and free ammonia.

If a solution of alkaline carbonate is mixed in the cold with decinormal acid in excess, and at once titrated back after the addition of the iodine salts, the blue colour constantly reappears in the solution which has become colourless. Approximately correct results are obtained if we take into calculation that quantity of thiosulphate which just suffices to keep the liquid colourless for some seconds. This disturbing influence of carbonic acid depends on the fact that it exerts at the same time a decomposing influence upon the iodine salts. To obtain accurate results it is therefore advisable, after adding the excess of decinormal acid, to expel the carbonic acid by ebullition, and then to determine the acid iodometrically in the liquid when completely cold.

* Zeit. für Angew. Chemie und Zeit. für Analytische Chemie.

As in the determination of the alkaline carbonates, it is judicious in the determination of the sulphides and hydrosulphides of the alkaline metals to boil the liquid after supersaturation with normal acid. If the expulsion of the sulphuretted hydrogen by boiling is omitted and the liquid supersaturated, the decinormal acid is at once mixed with a sufficiency of the solution of the iodine salts. On the addition of the solution of iodine salts, the sulphuretted hydrogen is decomposed according to the equation: $\text{KIO}_3 + 5\text{KI} + 3\text{H}_2\text{S} = 6\text{KI} + 3\text{H}_2\text{O} + \text{S}_3$, and iodine is eliminated corresponding to the excess of acid.

(To be continued).

THE PLAGUE OF FIELD-MICE IN THESSALY SUCCESSFULLY COMBATTED BY MEANS OF *BACILLUS TYPHI MURIUM*.

By F. LÖFFLER.

THE author, who has found a new bacteriological method of combatting the plague of field-mice by means of *Bacillus typhi murium* (the inciting organism of mouse-typhus), had last spring, in accordance with an invitation from the Greek government, the opportunity to prove his method on the large scale in Thessaly, where field-mice had been multiplying to a frightful extent and threatened to destroy the plentiful harvest of this season.

From the author's interesting report on his activity we learn that the Thessalian field-mouse, rather different in its appearance from our field-mouse (as accurate determination of the species will be given), is even more susceptible to the bacillus of mouse-typhus than our native field-mouse. In addition to these animals no other species seems to be susceptible to the bacillus. Dogs, horses, asses, goats, sheep, like men, are not susceptible to the infection.

The preparation of the nutrient liquid is effected in large 60-litre vessels like milk cans. Into these is put a decoction of straw, mixed with peptone and glucose, neutralised with sodium carbonate, and sterilised by three times boiling for two hours each in a current of steam. After the vessels had cooled down to about 40° they were infected with a pure culture of the bacillus and set aside at above 30°. In the course of two days the bacilli had been developed in the vessels in abundance. On the other hand, water (in portions of one litre each), was infected with pure cultures raised on agar which had congealed in a slanting position. Pieces of bread of the size of a finger-joint were saturated with these liquids rich in bacilli, and the pieces thus impregnated were thrust into the holes of the mice.

Although vegetation was luxuriant, and there seemed no reason why the mice should not prefer their natural food to any artificial substitute, the bread soon disappeared, and in a few days there were found dead mice which displayed the pathological characters of mouse-typhus, and which contained the characteristic bacilli of the disease in their organs. From day to day the result became more decisive, and the representatives of the Greek government gladly admitted the success of the new method.

The hopes that in the bacillus of mouse-typhus we have an effectual remedy against the plague of field-mice, which yearly occasions in all European countries damage amounting to millions, have proved fully justified. For the first time it has been thus found practicable to combat successfully a destructive form of vermin with bacteriological means.—*Centralblatt f. Bakteriologie und Chem. Zeitung*.

Certain Double Salts of Quinine.—E. Grimaux.—The author has obtained and examined the quinine chlorhydrosulphate, bromhydrosulphate, and iodhydrosulphate, and also the quinine chlorbrom- and iod-hydrophosphates. —*Comptes Rendus*, cxv., No. 17.

SUCROSE, DEXTROSE, LEVULOSE: THEIR QUANTITATIVE DETERMINATION WHEN OCCURRING TOGETHER.*

By F. G. WIECHMANN, Ph.D.

AN accurate method for the determination of sucrose, dextrose, and levulose, when occurring together, has long been sought for in sugar-chemistry, for such a method of analysis would prove valuable for the solution of many questions of interest and importance.

The solving of this problem,—a problem of acknowledged difficulty,† has been attempted by different workers and in various ways.

For some years past it has also engaged the attention of the writer, and in the *School of Mines Quarterly* (vol. xi., No. 3; vol. xii., No. 3), Columbia College, New York, are given some of his former studies on this subject.

The method of analysis there described,—a method based solely on gravimetric determination, yet awaits, in order to furnish results reliable under all circumstances, discovery of some agent whereby the complete destruction of either the dextrose or the levulose may be accomplished, while the sugar not destroyed shall remain entirely unchanged in its properties.

As the chances for immediate success in this direction did not seem very promising, the solution of the tempting problem was sought and found in another manner.

In recording in this paper the successful outcome of his quest, the writer desires to acknowledge his obligations to those who before him have attempted his task, and a critical study of whose labours has proved of value to the writer in his own researches. Furthermore, his sincere thanks are due to his assistant, Mr. E. C. Brainerd, for much valuable work most carefully and conscientiously performed in this investigation.

The method here to be described involves but three simple analytical operations: two gravimetric determinations, and one optical examination with the polariscope. The method is therefore easy and rapid of execution, and at the same time, with careful manipulation, yields most accurate results, as will appear from the various trials to which the method was subjected in order to determine its value and delicacy. A full record of these experiments follows the subjoined description of the method.

The Method.

Preparation of Solution.—If not already in solution, make of the sample to be examined a solution of arbitrary density. Of course, it goes without saying that this method is to be applied only in cases where no other optically active substances are present besides sucrose, dextrose, and levulose, and that care must be exercised that no preliminary treatment of the solution shall influence its original power of rotation.

The specific gravity of the solution above referred to is accurately determined by balance, and from this value there are calculated in the following manner the number of grms. of solution which contain 10·000 grms. of dry substance.‡

Ascertain the degree Brix corresponding to the specific gravity found. Divide 100 by the degree Brix; the quotient represents the number of grms. of solution, which contain 1·00 grm. of dry substance. This value is multiplied by ten, and the product represents the number of grms. of solution, equivalent to 10·000 grms. of dry substance.

This amount is weighed out, placed in an accurately graduated 100 c.c. flask, and the solution in the flask is made up to 100 c.c. with distilled water.

* From the *School of Mines Quarterly*, xlii., No. 3.

† Thus B. Tollens (*Kurzes Handbuch der Kohlenhydrate*, p. 90) :

"Sehr schwierig ist die Bestimmung, wenn Gemenge von Levulose mit anderen Glycosen wie Dextrose oder mit Rohrzucker vorliegen."

‡ This concentration is chosen because the specific rotary powers of the sugars, values needed in the calculation of results, vary with the concentration.

The determinations to be made are as follows:—

Optical Examination.—Some of the solution is placed in a water-jacketed polarisation-tube, a thermometer is inserted in the solution, and a reading on this solution is taken in the polariscope at the temperature of 20° C.

The reading thus obtained must be reduced to the basis of a reading made in a 100 m.m. tube.

Furthermore, if a sugar-polariscope has been used for the observation, the reading obtained must be transformed into circular degrees. With a polariscope using 26.048 grms. as the normal weight, the factor 0.346 is used for the sodium ray.

Gravimetric Determination before Inversion.—Of the 10 per cent solution weigh out an amount equivalent to 1.0 gm. of dry substance. Make this up to 150 c.c., and of this solution take 24.4 c.c., equivalent to 0.1628 gm. dry substance. Take 50 c.c. of Fehling solution,* heat to boiling; while boiling add the 24.4 c.c. of sugar solution and boil for three minutes.

Then remove from flame, add cold distilled water, previously boiled, in order to cool the solution and prevent a further deposition of cuprous oxide.

Filter through a weighed asbestos filter, wash first with boiling water, then with absolute ethyl alcohol, and finally with ether. Dry perfectly, cool and weigh.

Calculate the cuprous oxide to its equivalent of metallic copper, and from the copper thus found ascertain the amount of sucrose corresponding.† From this figure the total reducing-sugars by adding $\frac{x}{2}$ to the sucrose value indicated.

Gravimetric Determination after Inversion.—Of the original 10 per cent solution weigh off an amount equal to 5.000 grms. dry substance; invert with 4 c.c. of concentrated HCl (specific gravity 1.20) by heating on boiling water-bath up to a temperature of 67° C. and maintaining the solution at that temperature for five minutes. Then remove the flask, cool it and its contents to the temperature at which the flask was graduated, and then make the solution up to 100 c.c.

Of the solution thus obtained take 20 c.c. and neutralise with sodium carbonate; then make up to a volume of 150 c.c. with distilled water; of this solution take 24.4 c.c., equivalent to 0.1628 gm. of dry substance, and proceed precisely as previously directed. Determine the value found, as before, from the table; the result obtained represents the total sugars present, *expressed as sucrose*. From this amount subtract the *sucrose* value found by prior determination,‡ and the difference represents the amount of sucrose actually present.

The results thus obtained represent the polarisation, in a 10 per cent solution, of the three sugars combined; the total reducing sugars present; the amount of sucrose present.

In cases where the reducing sugars, i.e., the dextrose and the levulose together, exceed in amount the sucrose present, the gravimetric determinations before and after inversion should preferably be made according to E. Meissl's method for the determination of invert sugar (*Zeit. des Vereines für Rübensucker Industrie*, vol. xxix., p. 1034, and E. Wein *Tabellen zur Quantitativen Bestimmung der Zuckerarten*, Table No. IV.).

Calculation of the Results of Analysis.

This can be accomplished by algebra, or by allegation.

By Algebra.

Let—

a = amount of sucrose present.

b = amount of total reducing sugars present.

* Cupric sulphate cryst., 34.699 grms. in 500 c.c. water; Rochelle salts, 173.000 grms. in 400 c.c. H₂O; sodic hydrate, 50.000 grms. in 100 c.c. H₂O.

† Table published by the German Government, Law of 1887; also in Wiechmann, "Sugar Analysis," Table XI.

‡ That is, the amount as actually found by table prior to the addition of 1-20th.

x = amount of dextrose present.

y = amount of levulose present.

s = the specific rotatory power of sucrose, divided by 100.

d = the specific rotatory power of dextrose, divided by 100.

l = the specific rotatory power of levulose, divided by 100.

p = polarisation observed, expressed in circular degrees.

Then—

$$(as + xd) - yl = p.$$

$$(as + xd) = p + yl.$$

$$xd = p + yl - as.$$

$$x = \frac{p + yl - as}{d}.$$

Substituting this value of x in the equation—

$$x + y = b$$

there results—

$$\frac{p + yl - as}{d} + y = b.$$

$$p + yl - as + yd = bd.$$

$$yl + yd = bd - p + as.$$

$$y(l + d) = bd - p + as.$$

$$y = \frac{bd - p + as}{l + d}.$$

As y represents the amount of levulose, y deducted from b will give at once the amount of dextrose. Or, if preferred, the value of x can also easily be calculated independently.

Example—

Sucrose = a = 8.50.

Total reducing sugars = b = 1.50.

Polarisation, expressed in circular degrees = p = 5.6426.

Specific rotatory power of sucrose $\div$ 100 = s = +0.665.

Specific rotatory power of dextrose $\div$ 100 = d = +0.535.

Specific rotatory power of levulose $\div$ 100 = l = -0.819.

Dextrose present = x .

Levulose present = y .

$$(8.50 \times 0.665 + x \times 0.535) - (y \times 0.819) = 5.6426.$$

$$(8.50 \times 0.665 + x \times 0.535) = 5.6426 + (y \times 0.819).$$

$$0.535x = 5.6426 + 0.819y - 5.6525.$$

$$(1). \quad x = \frac{-0.0099 + 0.819y}{0.535}$$

$$(2). \quad x + y = 1.50.$$

Substituting the value of x found in equation (1) in equation (2) there results—

$$\frac{-0.0099 + 0.819y}{0.535} + y = 1.50.$$

$$-0.0099 + 0.819y = 0.8025.$$

$$1.354y = 0.8124.$$

$$y = 0.600.$$

Total reducing sugars present. . . . = 1.50

Levulose present = 0.60

Dextrose present = 0.90

By Allegation.

Example—

Determinations made on a 10 per cent solution.

	Per cent.
Sucrose present	= 66.0
Total reducing sugars present	= 34.0
Polarisation observed	= 2.8199
Polarisation due to the sucrose = 6.6	
$\times 0.665$	= 4.3890
Difference due to the 3.40 per cent reducing sugars	= 1.5691

$$\begin{array}{r} 34:100::1'5691:x \\ 156'91 \div 34 = -4'615. \\ +53'5 \quad \quad 35'75 \\ -81'9 \quad \quad -46'15 \\ \hline \quad \quad \quad 99'65 \\ \hline \quad \quad \quad 135'40 \end{array}$$

135'4:35'75::34:x=8'98 per cent of dextrose.

135'4:99'65::34:y=25'02 per cent of levulose.

Or else, having found the percentage of dextrose as above,—

	Per cent.
Total reducing sugars	= 34'00
Dextrose present	= 8'98
Levulose present	= 25'02

As to reporting the nature of the reducing sugars, the analysis of course only warrants the stating of the actual amounts of sucrose, of dextrose, and of levulose as found.

Should it, however, be so desired, equal quantities of dextrose and levulose might be considered as present in the form of invert sugar.

The dextrose or the levulose, of whichever one least is found, might be regarded as combined with an equal amount of the other, forming invert sugar, and any excess over the amount so disposed of could be reported as free or uncombined dextrose, or levulose, as the case might be.

(To be continued).

ON IRON RUST POSSESSING MAGNETIC PROPERTIES.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.
(Concluded from p. 232).

No. 12.—Rust from Cast-Iron Gas Plug-Box.

14'26 grms. were passed through a No. 60 sieve and found to be wholly magnetic.

This rust was in the form of thick scales, strongly magnetic, and when broken open presented in places a crystalline structure. Under the microscope some of the crystals could be recognised as more or less well formed octahedrons of a bluish-black metallic colour and lustre, and they doubtless were crystals of magnetite. The scales of rust were found to have in one case a specific gravity of 4'23 at 15° C.

No. 13.—Rust from Old Gate Hinges.

These had been left lying in an open barrel; the powdered rust was wholly magnetic.

No. 14.—Rust from Sydney Water Mains.

The Sydney water mains choke up very rapidly with "rust," and have in consequence to be replaced from time to time. The deposit consists of hydrated sesquioxide of iron, iron monoxide, silica, alumina, lime, sodium chloride, &c., organic matter, and some free sulphur; the last is derived from the reduction of sulphates by the organic matter.

Fifty grms. of the rust from the interior of some 6-in. mains, kindly supplied to me by Mr. Houghton, gave, when crushed in a porcelain mortar and passed through a No. 60 sieve, 9'33 grms. of magnetic particles.

Fifty grms. from another specimen less finely ground gave 6'79 grms. of magnetic oxide.

A third sample was passed through a No. 90 sieve, and then ground in an agate mortar, but it gave much trouble

from clogging together into cakes. 22'719 grms. of this were washed in a Knop's soil-washing apparatus. Some of this was washed away and lost from its extreme lightness, but the 4'02 grms. of black powder left were entirely magnetic.

No. 15.—Rust from Decayed Gas-Pipes, Melbourne.

Mr. G. Foord, F.C.S., of the Melbourne Mint, examined in 1867 certain gas-pipes which had been almost wholly converted into ferric hydrate. (See "Decay of Gas-Pipes in Certain Soils," G. Foord, *Transactions Royal Society of Victoria*, 1874).

It was found that the gas-pipes near the site of the Melbourne Old Exhibition were subject to very rapid decay. The site is one hundred feet above high water mark of Hobson's Bay. The porous soil of harsh, nearly white, mottled permeable clay is also favourable to drainage by percolation, and described as free from any constituent likely to corrode the pipes unduly.

He found the specific gravity to be—

A.—Undecayed portions	5'99
B.—Decayed portions	2'57
C.—Portion with thin inner shell of metallic iron ..	2'88
D.—Grey cast-iron for comparison	7'10

"The decayed portion had lost to some extent, but not altogether, its magnetic properties. It is easily reduced to a greenish brown powder, approaching the tint of raw umber. On solution in hydrochloric acid it evolves no hydrogen, a fact which shows that it contains no residue of iron in the metallic state; when thus dissolved it leaves a bulky residue of graphite, with silicon, carbon, and sulphur compounds of iron and manganese."

"The converted portion when newly taken from the ground is soft, but hardens on exposure."

Further details are given, but the above are sufficient for my present purpose, except that it may be stated that Mr. Foord attributes the rapid oxidation and decay to the action of soluble chlorides in the soil, as has been stated to be the cause in other places.

A piece of the decayed pipe was forwarded by Mr. Foord in 1869 to the late Dr. Smith, Professor of Physics in the Sydney University, who gave it to me some years ago when I was examining some cast-iron which had been acted upon by sea-water. (*Journal Royal Society of New South Wales*, vol. xiv., 1880).

The fragment resembles a curved shell-like piece of limonite. On crushing, it yields an ochre-coloured powder, which is in part attracted by the magnet, but free from particles of metallic iron. Another piece weighing 7'397 grms. yielded a little iron to iodine in potassium iodide, but was still wholly magnetic after the removal of the metallic iron. Other portions did not yield any iron to iodine in potassium iodide.

No. 16.—Rust from Hot-Water Pipe, Prince Alfred Hospital, Sydney. An ordinary 14-in. pipe.

Of a red-brown colour and feebly magnetic.

No. 17.—Rust from Cold-Water 14-in. Pipe, Prince Alfred Hospital, Sydney.

Partly magnetic. The non-magnetic portion contains much organic matter.

No. 18.—Rust from Screw and Nail, which had been exposed for a few months on a window sill.

They were both covered with a thin coat of dark brown oxide. The rust from both was attracted by the magnet, but not wholly; the quantity was small, and no attempt was made to weigh or estimate the amount.

19.—Rust from Old Bolt.

A small part of this was non-magnetic, but became feebly attracted after boiling in water.

* From the *Transactions of the Australasian Association for the Advancement of Science*, Hobart Meeting, 1892.

The writer has on various occasions cited the skin of magnetic oxide on meteorites as a proof of the high temperatures to which they have been subjected in their passage through the atmosphere; but in some cases this may perhaps have been found in the ordinary way, inasmuch as the foregoing experiments seem to show very clearly that the oxides yielded by the atmospheric rusting of iron may also be magnetic.

Experiments on the Rusting of Iron.

While the volume has been going through the press I have been able to obtain additional results from certain experiments which were going on when the paper was read, especially those upon sheet iron, nails, &c., which had been placed out to rust or immersed in cylinders of distilled water, &c.

The results do not differ from those already obtained and stated when the paper was read, but the extra time has enabled me to get thicker and heavier deposits of oxide, which are more satisfactory than thin films.

Black sheet iron was scoured with pumice-stone until perfectly bright, clean, and free from scale, and cut into strips 7×2 inches. The strips were then put up into lots of about 1 lb. each.

Experiment No. 1.—A hole was punched in each strip and a bundle of them suspended by a bright iron wire outside a window on September 11, 1891, when they weighed 456 grms. On February 16, 1892, *i.e.*, after nineteen weeks' exposure, these were scraped with a horn spatula and 2.14 grms. of rust obtained, of which only 0.184 grm., or 8.6 per cent, was non-magnetic. The colour of rust was ochrey outside and black inside.

Experiment No. 2.—A second lot of 457 grms. was suspended in the same way on the roof of the chemical laboratory. On February 16, 1892, *i.e.*, after nineteen weeks' exposure, these also were scraped with a horn spatula and yielded 6.6 grms. of rust, of which only 0.775 was non-magnetic, or 11.7 per cent. The rust was of the usual colour outside, but nearly black underneath.

Experiment No. 3.—A third bundle of sheets, weighing 453 grms., was placed in a 24-oz. stoppered cylinder of boiled distilled water on September 11, 1891. This iron was scraped on May 27, 1892, after thirty-six weeks' action, with a horn spatula, and brushed with a new nail-brush, and yielded 2.604 grms. of blackish oxide, of which the whole was attracted by the magnet.

Experiment No. 4.—A further bundle of 453 grms. was placed in a similar stoppered cylinder of unboiled distilled water, treated in the same way as Nos. 2 and 3, and on the same dates. Yielded 0.694 grm. of dark brown oxide, wholly lifted by the magnet.

Experiment No. 5.—453 grms. of strips were similarly placed in a cylinder of tap water on May 27. They were taken out, dried on a water bath, scraped with a horn spatula, and carefully brushed; the rust weighed 0.538 grm.; it was of a dark brown colour and wholly attracted.

Experiment No. 6.—A bundle of strips, weighing 449 grms., was placed in cylinder of distilled water charged with carbon dioxide. Treated in the same way as the others and on the same dates. This yielded 0.545 grm. of a dark yellowish brown colour. Some of the oxide in this case was in the form of brown iridescent films floating in the water. These brown films were also found to be magnetic after boiling; they were also found to yield no blue colouration with potassium ferricyanide added to their solution in hydrochloric acid. In all the other cases (1 to 5) the loose oxide floating in the water and attached to the iron was black.

Experiment No. 8.—453 grms. of bright 2 in. wire nails were exposed in a photographic dish on a window sill from September 11, 1891, to February 16, 1892. These nails were moistened from time to time, but not kept constantly wet. On scraping off the rust with a horn spatula, 7.79 grms. of rust were obtained, the whole of which was magnetic.

Experiment No. 9.—453 grms. of 6-in. bright wire nails were similarly exposed and treated at the same time. These nails only yielded 4.03 grms. of rust, which was also wholly magnetic. The smaller surface exposed by the larger nails accounts for the smaller weight of rust produced.

Experiment No. 10.—On September 21, 1891, 906 grms. of bright 6-in. wire nails were put out on a window sill (facing W.) in a new photographic dish, and covered with distilled water. After three days, *i.e.*, on the 24th, they were covered with loose ochrey rust which washed off readily, but under this and filling the striæ of the nails was a film of black oxide. When scraped on February 16, 1892, with a horn spatula, they yielded 4.03 grms. of rust of a dark brown colour, and entirely attracted by the magnet.

Experiment No. 11.—At the same time and place 1½ lbs. of bright 2½-in. wire nails were also put out in a photographic dish with the same result, except that there was very much more of the black oxide present.

On turning over the nails Nos. 10 and 11 on the 26th, *i.e.*, after five days' exposure, it was found that, while covered more or less completely with ochrey rust on the upper surface, the lower surfaces of the nails (which were completely immersed in the water) were free from it, but coated instead with a closely adherent film of black oxide, due apparently to the fact that, while there was sufficient oxygen on the exposed side of the nails to form both the red or ochrey and black oxide on the lower side (completely immersed in water) the oxidation did not go beyond the first stage. On February 16, 7.79 grms. of entirely magnetic rust were obtained.

The total amount of rust furnished by this experiment and No. 10 was much more than the weights given. The loose rust in the dishes was not weighed, because it was mixed with grit and dust which had fallen into the dishes during their exposure.

Experiment No. 12.—Some sheets of clean iron were also placed out, but not moistened. The rust was much darker in colour than that from Experiments 10 and 11, being of a dark reddish brown when scraped off with a horn spatula and powdered. The oxide weighed 2.14 grms., of which 0.184 was non-magnetic.

Experiment No. 13.—On September 21, 1891, 736 grms. of bright 6-in. wire nails were placed in a stoppered cylinder of hot and freshly boiled distilled water. In the course of a day or two they were coated with black oxide. On May 31 the oxide was collected, but only amounted 0.131 grm., which was feebly magnetic.

Experiment No. 14.—702 grms. of bright 6-in. wire nails were put up with distilled water charged with carbon dioxide. Gave only 0.211 of rust, of which but a small part was magnetic.

Experiment No. 15.—On September 22, 1891, 433.5 grms. of bright wire nails were placed in a stoppered cylinder, and dry ozonised oxygen from a Siemens tube passed in for twenty minutes. These nails were hardly rusted, and there was insufficient rust to remove.

Experiment No. 16.—415.3 grms. were also put up in the same way, and moist ozone passed in for about twenty minutes. Yielded on May 31, 1892, 1.437 grms. of highly magnetic oxide.

The absence of metallic iron was in these cases proved by grinding it in agate mortar, and in certain cases also by means of iodine.

Literature.

Although the results of previous investigators should usually have precedence, they are given at a later stage of this paper mainly because most of my experiments were carried out before I had time to fully look up the literature of the subject. The immense number of publications and amount of matter to be gone through nowadays is so overwhelming that if, in all cases, the necessary searches were to be made before experimenting, many questions which crop up would never reach the experimental stage at all.

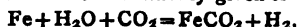
In the first instance I had, from want of time, to be content with reference to the chemical dictionaries and other standard works on chemistry, and as they were silent upon this subject, or stated that there was only one oxide of iron possessing magnetic properties, I went on with the experiments, and they were practically finished before I was able to go through the journals devoted to chemistry and allied subjects.

From the quotations which follow it will be seen that the views of the older chemists more closely correspond with my results than those of some of the more recent writers.

Most modern writers state that rust is non-magnetic, and is formed only in the presence of air, moisture, and carbon dioxide as follows:—

- (a) $\text{Fe} + \text{CO}_2 + \text{O} = \text{FeCO}_3$
- (b) $2\text{FeCO}_3 + \text{O} = \text{Fe}_2\text{O}_3 + 2\text{CO}_2$
- (c) $\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} = \text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O} = \text{rust}.$

This of course may more or less explain the reactions, but it evidently is too neat and complete, inasmuch as it does not account for the large proportion of magnetic oxide which always appears to be present in ordinary rust. Another reaction commonly given is—



and that the FeCO_3 formed takes up more CO_2 and is converted into the soluble acid carbonate, which in turn is converted into the insoluble ferric hydrate ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) or rust, and that the CO_2 is free to act again, but this is equally imperfect. Mendeleeff ("Principles of Chemistry," London, 1891, p. 321), amongst modern writers, recognises the fact that rust contains both ferrous and ferric oxides, but makes no mention of its magnetic properties.

In looking up the matter reference was first made to the later publications, but it was only in those published over thirty years ago that anything was met with really bearing upon the subject, the most interesting and valuable being the note by Mr. Robbins in the CHEMICAL NEWS for 1859, and the paper by M. Sarzeau in 1860, also in the CHEMICAL NEWS; both of these, however, seemed to have been ignored or overlooked by late writers.

The following quotations are arranged according to their dates of publication:—

It is stated in the "Dictionary of Chemistry and Mineralogy," by A. and C. R. Aiken, 1807, on p. 612, that "The common rust which collects upon hammered iron by exposure to air and moisture, and which in time corrodes the thickest bars, is not the simple oxyd, but a carbonated oxyd, or a compound of iron, oxygen, carbonic acid, and water, and is not of itself magnetic, unless mixed with fragments of iron detached by the rusting."

It is stated, too, that iron will oxidise and hydrogen be given off "even at the common temperature of the air, but the oxyd will then be in the form of a black powder, and will not exhibit that glossy appearance which it does in the former method," i.e., when steam is passed over red-hot iron. "The preparation called martial æthiops is iron oxidated by water, and was first made by Lemery the younger" by covering a quantity of clean iron filings with water, and stirring from time to time. "After a while bubbles of hydrogen constantly rise from the mass, and the vessel becomes full of a very fine black powder. This black powder is iron in the first or lowest state of oxidation or sub-oxyd; it is strongly magnetic, but has a constant tendency to absorb an additional quantity of oxygen from the air or any other substance by which it loses its magnetic property, changes from black to yellow or red, and acquires very different chemical characters."

Further, "Von Mons, having prepared a quantity of this black sub-oxyd, heated it in a retort to drive off the superfluous moisture, but on taking it out "a spontaneous motion or heaving took place through the mass; it became so hot as to burn a thick double paper in contact with it, and the whole in a few minutes was converted into the red or perfect oxyd or saffron of Mars."

Leopold Gmelin, in his "Handbook of Chemistry," vol. v., p. 185, Cavendish Society, 1851, says:—"Iron covered by a thin layer of water and exposed to the air is converted into the hydrated sesquioxide; ammonia is also formed."

"If the iron be covered by a deeper stratum of water so that the transference of the oxygen of the air through the water to the iron may take place more slowly, a formation of black hydrated ferroso-ferric oxide takes place, because hydrated ferric oxide, as it slowly forms, induces the iron to decompose the water and form ferrous oxide, with which the ferric oxide then unites.—(Wöhler).

Page 186: "Beneath the flocculent hydrated sesquioxide of iron there is formed a thin black crust (of ferroso-ferric oxide?) which adheres firmly to the iron."

"When cast-iron of this description (i.e., mixed grey and white) is exposed to the action of a mixture of seventy-five measures of aerated water and one measure of a saturated solution of chloride of sodium and carbonate of sodium, oxidation begins in a minute, and thus is formed—first, whitish hydrated ferrous oxide and hydrated ferroso-ferric oxide, which at some distance from the iron are converted into hydrated ferric oxide, and afterwards carbonate and silicate of ferrous oxide, the latter being produced by the oxidation of silicide of iron."

Page 186: 6. "At ordinary temperatures, and out of contact of air, iron does not decompose thoroughly boiled water, unless it is in contact with more electro-negative bodies, as with previously formed ferric oxide, mercury, &c. In this case, and likewise when the liquid is heated to 50° or 60°, a feeble evolution of hydrogen takes place, and ferroso-ferric oxide appears to be formed.—Hall, 2 *J. C. S.*, vol. vii., p. 55. Guibourt, *Ann. Chim. Phys.*, vol. xi., p. 43).

Page 187: "Ferrous oxide decomposes water by continued contact, and is converted into ferroso ferric oxide."

Page 188: "If a ferrous salt be precipitated by ammonia instead of by potash, the precipitate, after long standing, gives off hydrogen gas, becomes gradually darker in colour, and when dried in the manner above described is converted into black ferroso-ferric oxide containing ammonia.—(G. Schmidt, *Ann. Pharm.*, xxxvi., 101).

"Dried ferrous hydrate is not magnetic (Liebig and Wöhler), and on exposure to the air it is instantly converted into ferric oxide. The heat often rises to redness."

Page 193: "Iron black or *Æthiops Martialis Lemeryi* is a mixture of ferric and ferrous oxides in different proportions, according to the mode of preparation, and is partly hydrated."

Page 194: "Hydrated *Æthiops*.—Iron filings are placed in a wide vessel covered with a deep stratum of water, exposed to the air for a considerable time with frequent stirring, the light black powder is decanted from the still unoxidised iron from time to time, collected on a filter, and rapidly dried. This preparation is doubtless identical with the black hydrate of ferroso-ferric oxide already described."

The above quotations are given because they give a more accurate account of the process of the oxidation of iron than some of the more modern writers.

J. Robbins, in a note on "Magnetic Peroxide of Iron," CHEMICAL NEWS, vol. i., 1859, p. 11, states that he ignited some black magnetic oxide of iron on platinum foil over a spirit lamp. "After ignition the black oxide had apparently become converted into the common red peroxide of iron, but on applying the magnet, to my great astonishment I found that its magnetic properties remained unimpaired. The next question to determine was whether it was still a combination of the two oxides having undergone some molecular change, or whether the protoxide had not become converted into peroxide by absorption of oxygen from the atmosphere. I therefore dissolved some of the red powder in hydrochloric acid, and to the solution added some ferridcyanide of potassium, but not a

trace of the protosalt was indicated by that reagent. The magnetic peroxide may also be conveniently prepared by fusing together for some minutes the common black oxide with three or four times its weight of nitrate of potash. Prepared in this way it is more readily dissolved by hydrochloric acid than that obtained by simple ignition.

"I have searched various chemical works, but can find no mention of a magnetic peroxide of iron. I therefore presume that this peculiar compound has escaped observation."

M. Sarzeau (CHEMICAL NEWS, i., 1860, p. 137, and *Journ. de Pharm. et Chemis.*, Jan. 23, 1860), in describing a method of preparing aerated water from plates of iron placed in a solution of carbonic acid in water at 50° F., says:—"We obtain a liquid with well-marked inky flavour, and which has all the properties of a solution of a protosalt of iron. If the liquid be heated it is at first turbid, and then becomes milky, afterwards ochrey, and at last when it boils it suddenly changes to a deep brown. On cooling it deposits a substance of the same colour, which, separated by filtration, dried in the air, and dissolved in hydrochloric acid, gives a mixture of protochloride and perchloride of iron. If a magnet be brought in contact with the brown matter when dry it is found to adhere, showing that by heating a solution of carbonate of iron magnetic oxide is formed."

I did not come across the accounts of the experiments by Mr. Robbins and M. Sarzeau until my own were practically completed, as they are not quoted in any of the Chemical Dictionaries and works of reference, but I have since repeated them, and can confirm their results.

Robbins's experiment of heating finely-powdered magnetite was repeated on several samples of magnetite, and in each case the resulting sesquioxide of iron was found to be wholly attracted by a magnet, although no trace of ferrous oxide could be detected in the red powder by dissolving in hydrochloric acid and adding potassium ferricyanide.

The powder is still attracted by the magnet when hot, but more strongly on cooling, as in the case of metallic iron.

M. Sarzeau's results were confirmed by converting precipitated ferrous carbonate into the acid soluble carbonate by passing carbon dioxide through water containing ferrous carbonate in suspension. On warming this solution or exposing it to the air the carbon dioxide escaped, and a dark-coloured precipitate was thrown down. Usually this was found to be attracted by the magnet, but not always. On further warming and longer exposure it gradually acquires a buff colour and becomes magnetic, although not strongly so, but seen by acting upon it with the magnet under water. A temperature of about 70° C. seemed to be the best. At from 270° to 290° C. the colour became red, the magnetic properties being retained even after ignition; the solution in hydrochloric acid showed no trace of ferrous salt with potassium ferricyanide.

There is sometimes a little difficulty in obtaining the magnetic sesquioxide by this process. The cause is not quite clear, but is probably due to the ferrous carbonate not having in all cases been thoroughly washed free from other salts.

Dr. F. Grace Calvert, in a paper on the "Oxidation of Iron" (*Journ. Chem. Soc.*, 1871, p. 198, and CHEMICAL NEWS, 1871, vol. xxiii., p. 98), gives the following analysis of rust:—

	Conway Bridge.	Llangollen.
"Iron sesquioxide	93.094	92.900
Iron protoxide	5.810	6.177
Iron carbonate	0.900	0.617
Silica	0.196	0.121
Ammonia	—	—
Calcium carbonate	—	0.295 "

No remark is made as to whether the rust was magnetic or not, although it probably was; and the same remark

doubtless applies equally to the rust described by Mr. Cowper and Dr. F. Muck, as follows:—

"Oxidised Iron from the condenser of H.M.S. *Spartan*," by Richard Cowper, A.R.S.M. (*Journ. Chem. Soc.*, 1882, vol. li., p. 256.)

The specimen was found in part of the tank of a surface condenser, and which in use had been constantly subjected to the action of sea-water at a temperature not exceeding 100° F.

It consisted of a brownish substance, in which were embedded numerous shining black particles, and resembled very much in appearance a piece of rusty grey pig-iron. Sp. gr., 2.63 only, and extremely friable. A full analysis is given; there was 42.33 per cent of ferrous oxide and 2.21 per cent of ferric oxide present.

He states also that a specimen of ordinary iron rust scraped from some cast-iron (which had rusted in moist air) gave 65.42 per cent ferric and 7.42 per cent of ferrous oxide.

Dr. F. Muck (*Stahl und Eisen*, viii., p. 837—41, also *Journal Iron and Steel Institute*, 1889, i., p. 385), states that the rust in a boiler formed in pits near the feed-pipe had a fungoid form, and dried at 100° C.; it had the following composition:—

Fe ₂ O ₃	66.84
FeO	23.24
CaO	2.60
MgO	0.39
SiO ₂	1.18
SO ₃	0.28
CO ₂	2.32
C	0.22
H ₂ O	2.75
Organic	0.18

The organic matter was soluble in ether, and probably derived from the lubricants used. "The rust therefore mainly consists of magnetic oxide."

Prof. W. Spring (*Bull. Soc. Chim.*, vol. l., pp. 215—18, and *Journ. Soc. Chem. Industry*, Nov. 30, 1888), says that the cause of iron rails rusting less rapidly when in use than when not subjected to traffic is not due to the vibration of passing trains, nor to currents of electricity, nor to a film of grease derived from the engine and carriages, but rather to the formation of a layer of magnetic oxide on their upper surface formed by the pressure of the wheels on the moist ferric oxide with which they naturally become coated. He mixed damp ferric hydrate with minute particles of metallic iron, and subjected the mixture to a pressure of 1000 to 1200 atmospheres, and found that the two adhered, and that the hydrate became black to the depth of 0.5 m.m. Analysis showed that magnetic oxide had been formed. He also found that the rust taken from a rail contained some magnetic oxide and a little free iron mixed with the ferric oxide, and came to the conclusion that rails in use are protected by the magnetic oxide thus formed by the pressure, just as in the case of iron artificially coated with magnetic oxide.

From the foregoing experiments, and those detailed in a note upon the "Occurrence of Magnetite in Certain Minerals and Rocks," it appears:—

1. That native sesquioxide of iron and its hydrates, such as hæmatite, goëthite, limonite, &c., are themselves non-magnetic, i.e. to an ordinary bar magnet, but may contain some magnetite.

2. That sesquioxide of iron obtained by precipitation from the acid carbonate of iron, and probably from other salts of iron, is magnetic, or may be rendered magnetic by long boiling or by heating at various temperatures up to redness, and that such magnetic sesquioxide is free from any monoxide.

3. That magnetic sesquioxide of iron free from monoxide can be obtained by heating the magnetic oxide, as first shown by Robbins.

4. That ordinary rust produced by the oxidation of metallic iron is usually magnetic, and often polar. Magnetic rust usually contains more or less ferrous oxide, and may accordingly be regarded as $x\text{FeO}$, $y\text{Fe}_2\text{O}_3$, *i.e.*, varying mixtures of FeO and Fe_2O_3 , and of their hydrates, being well known to possess magnetic properties, although in other cases the rust may be quite free from monoxide and yet be magnetic.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 28th, 1892.

Dr. J. H. GLADSTONE, F.R.S., Past President, in the Chair.

Mr. G. H. WYATT was elected a member of the Society.

The Discussion on Mr. Williams's paper "*On the Relation of the Dimensions of Physical Quantities to Directions in Space*," was opened by Prof. PERRY reading a communication from Prof. FITZGERALD, President.

The writer said Mr. Williams disagreed with the suggestion that electric and magnetic inductive capacity are quantities of the same kind, principally because he had not got over the curious prejudice that potential and kinetic energy are different. No theory of the ether could be complete unless it reduced its energy to the kinetic form. Electric and magnetic inductive capacity would probably be found to be similar in the ether and ultimately have the same dimensions. The analogies were not yet complete, but only in respect of *matter* was it probable that any difference existed between them. Diamagnetism corresponded to electrostatic induction, but paramagnetism had no definite electrical analogue. He was inclined to regard the phenomena of paramagnetism as connected with the arrangement of the material molecules, whilst diamagnetism depended on the electric charges on those molecules. So far no matter had been found which conducts magnetism, and such may not exist in our universe, but it may be gravitationally repelled by matter as we know it.

Mr. MADAN remarked that in the first part of his paper Mr. Williams recognised that dimensional formulæ were originally change ratios, but puts this aside for the higher conception which regards these formulæ as expressing the nature of the quantity. Fourier showed how to find the dimensions of units by making the size of the fundamental units vary; but k (specific inductive capacity) did not vary with the fundamental units, for it was merely the ratio of the capacities of two condensers, and therefore, by Mr. Williams's definition, a pure number. It was difficult, he said, to see how k could have dimensions, but Mr. Williams regarded it as a physical quantity, and therefore possessing dimensions. The object in giving dimensions to k and μ seemed to be to get over the double system of units.

Mr. Madan did not think that dimensions could express the nature of physical quantities, and said differences of opinion existed amongst authorities on this point. For example, Dr. J. Hopkinson at the last British Association meeting said that because a coefficient of self-induction had the dimensions of length it must be a length, whilst other learned professors objected to this view. Even if one admitted that dimensions are a test of the nature of physical quantities, it was not necessary that the two systems of units should be identical. The connecting link between the two systems was $Q = Ct$, and the validity of this equation had been questioned. If this objection be confirmed, then there would be no current in electrostatics, and no Q in the electromagnetic system, and the units would not clash.

Referring to dynamical units, Mr. Madan pointed out that two units of mass were used in astronomy, but astronomers got over the difficulty by using a coefficient. Dimensional formulæ, he said, are the result of a convention that certain definitions should hold true generally, but they contain no further information respecting the nature of the quantities beyond that involved in those definitions. As an example of the inability of such formulæ to express the nature of quantities, he pointed out that whilst physical differences were known to exist between + and - electricity, the dimensional formulæ showed no signs of such differences.

Prof. RÜCKER said every correct physical equation consisted of a numerical relation between physical quantities of the same kind, and might be written either as a mere numerical equation or as a relation between the physical quantities themselves. The equation $2 + 1 = 3$ may correspond to 2 feet + 1 foot = 3 feet, and the latter may be written $2[L] + 1[L] = 3[L]$, where $[L]$ represents the unit of length. So far as he was aware, nobody but a recent writer in *The Electrician* had denied that in such an equation $[L]$ represented a concrete quantity. Maxwell explicitly stated that it does in his article on "Dimensions" (*Encycl. Britt.*) and elsewhere, and Prof. J. Thomson in his paper on the same subject makes no statement contrary to this. The above equation might also be written 2 [feet] + 1 [foot] = 1 [yard]. Another equation, involving time, is 60 [secs.] = 1 [minute], and dividing one by the other one gets—

$$\frac{2}{60} \left[\frac{\text{foot}}{\text{sec.}} \right] + \frac{1}{60} \left[\frac{\text{foot}}{\text{sec.}} \right] = 1 \left[\frac{\text{yard}}{\text{min.}} \right].$$

A difficulty was felt here in understanding what dividing a foot by a second meant; but this difficulty, Prof. Rucker considered, was not greater than that involved in dividing an impossible by a real quantity—a very familiar analytical device. Reasons for regarding the symbols $\left[\frac{\text{foot}}{\text{sec.}} \right]$ as legitimate were then given.

Prof. HENRICI said the communication under discussion was one of the most important contributions to physical science which he had come across for a long time. Such difficulties as presented themselves in the paper arose from its fundamental character. The author had attempted to express all physical quantities in terms of three, but quantities may exist which cannot be completely represented in terms of L , M , and T . The tendency of modern mathematics was to express everything dynamically. Mathematicians had long been in the habit of using quantities which were neither numbers nor concretes in the ordinary sense, and different kinds of algebra, with units not understandable, had been developed. If a quantity a times a unit u , be multiplied by b times another unit, v , the result is expressed by $a \cdot b \cdot u \cdot v$; where $a \cdot b$ is a number, and $u \cdot v$ a new unit, which may or may not be physically interpretable. The interpretation of a product depended on the meaning attached to "multiplication," and if this be restricted to "repeated addition" the range is very limited. The narrow conceptions concerning multiplication acquired at school could only be removed by a careful study of vectors. Mr. Williams had treated his subject by vector methods, but a few traces of quaternions remained which might be omitted. To truly understand the subject, vectors must be treated vectorially; dimensions might then show the nature of the quantities involved. The system adopted in Mr. Williams's paper was probably the best attainable at present, but he (Prof. Henrici) looked forward to the use of a more fundamental quantity than the vector—viz., "the point"—as the ultimate basis. Grassmann had worked out a "point calculus" in 1844 which was republished in 1880. Quantities more complex than vectors, viz., rotors, screws, motors, &c., had been used with advantage by Clifford, Ball, and others.

Dr. SUMPNER thought the first ideas of students on the

subject of dimensions were that they represented the nature of the quantities, but could not see why every quantity should be expressed in terms of L, M, and T. Prof. Rücker's paper on "Suppressed Dimensions" had cleared up several important points, and he (Dr. Sumpner) now considered that every quantity must be expressed in terms of a unit of the same kind as itself. He viewed Mr. Williams's attempt to express everything in terms of L, M, and T as rather a retrograde step.

The discussion on Mr. Williams's paper was adjourned, and

Dr. YOUNG made some remarks on Mr. SUTHERLAND's communication "*On the Laws of Molecular Force*."

Mr. Sutherland, he said, thought that Ramsay and Young's law, $\delta p/\delta T = f(v)$, is not correct for compounds in the liquid state. Barus, however, has proved that several liquids, including ether, only showed variations from the law at extremely high pressure. After writing the equation of the virial in the form $p v = RT\phi(v) + v\psi(v)$; where $v\psi(v)$ stands for the internal virial term. The author of the paper had shown that $v\psi(v)$ ought to be constant, but finding it not constant in the case of ether, &c., he attempted to explain the discrepancies by the formation of pairs of molecules at small volumes. Other substances, such as nitrogen and methane, were supposed to follow the law. This, Dr. Young said, could not be accepted as proved, for the range of volumes over which the experiments had been made was only small, and methane was difficult to prepare pure. After criticising the use of two and sometimes three "characteristic equations" for the same substance, he went on to show that the formulæ given in the paper by which the critical temperatures, pressures, and volumes might be calculated, lead to results differing from experimental numbers by quantities greatly in excess of experimental errors. Experiment also showed that capillarity had little or no effect on the determination of critical constants. Speaking of critical volumes, he pointed out that MM. Calletet and Mathias had published a method of finding critical densities which gave very accurate results.

Mr. Sutherland's conclusions respecting Van der Waal's generalisations were practically identical with those expressed by Dr. Young in his paper on the subject read before the Society last year. The views as to the nature of the various kinds of "pairing" mentioned in Mr. Sutherland's paper were open to various objections, for his "physical pairing is supposed to produce more effect on the "characteristic equation" than true chemical pairing. In his (Dr. Young's) opinion, the idea of physical pairing appears somewhat speculative, and requires further elucidation.

A paper "*On the Determination of the Critical Density*," by Dr. YOUNG and Mr. G. L. THOMAS, B.Sc.; and two papers "*On the Determination of Critical Volume*," and "*On the Boiling-points of Different Liquids at Equal Pressures*," by Dr. YOUNG, were taken as read.

The first paper gives an account of results obtained by Calletet and Mathias's method, based on the fact that the means of the densities of a substance in the states of liquid and saturated vapour when plotted with temperature lie on a straight line which passes through the critical point.

In the paper on "Critical Volumes," the above-mentioned method is again referred to, and results obtained thereby accepted in preference to those given by the author in his paper on "Generalisations of Van der Waals, &c.," read before the Society about a year ago. The alcohols do not strictly follow the straight line law. Revised tables of critical volumes, densities, pressures, and temperatures are given, and it is pointed out that for many substances the ratio of the actual critical density to the theoretical density (for a perfect gas) is about 3.8.

The paper on "Boiling-points of Different Liquids at Equal Pressures" contains a comparison of the accuracies with which a formula for the relation between the boiling points given by M. Colst (*Compt. Rend.*, cxiv., p. 653) and

one by Ramsay and Young (*Phil. Mag.*, Jan., 1886) accord with experimental results. The author concludes that the latter formula shows the best agreement, but that of M. Colst is satisfactory under certain conditions.

The further discussion of Mr. Williams's and Mr. Sutherland's papers was adjourned till the next meeting.

NOTICES OF BOOKS.

Commercial Organic Analysis; A Treatise on the Properties, Proximate Analytical Examination, and Modes of Assaying the various Organic Chemicals and Products employed in the Arts, Manufactures, Medicine, &c. With Concise Methods for the Detection and Determination of their Impurities, Adulterations, and Products of Decomposition. By ALFRED H. ALLEN, F.I.C., F.C.S., Past President of the Society of Public Analysts, Public Analyst for the West Riding of Yorkshire, the Northern Division of Derbyshire, the County Borough of Sheffield, &c. Second Edition, Revised and Enlarged. Volume III., Part II., *Amines and Ammonium Bases, Hydrasines, Bases from Tar, Vegetable Alkaloids*. London: J. and A. Churchill, 1892, pp. 584.

THIS volume, so long expected, will be eagerly welcomed by the chemical public of all English-speaking countries. All readers acquainted with the earlier edition will know that the author has not—as does Fresenius for mineral matters—confined himself to the most approved methods for the recognition and determination of organic chemical individuals. The nature of his subject obliges him to deal not only with compounds but with mixtures, natural or artificial, and in the latter case often fraudulent. Hence much pharmacological matter has been of necessity introduced. The result as a whole must be pronounced exceedingly useful.

The most valuable and important section of the volume before us is that which discusses the vegetable alkaloids so interesting therapeutically, dietetically, and toxicologically. Here Mr. Allen, in addition to his own researches, has collected all trustworthy results up to the present date, and has given us a survey of this class of bodies, hitherto unequalled in our literature.

In these days, when the infectious mania known as anti-vivisectionism is experiencing a recrudescence, it may not be amiss to ask how, in the absence of experiments upon animals could the detection of the poisonous alkaloids ever have been studied? Some of the most dangerous, such as aconitine, cannot be certainly recognised by any chemical test. It is not improbable that secret poisoning may revive in this country owing to the increased difficulties thrown in the way of detection, no less than to the discovery of the toxic action of the ptomaines.

We are commonly told that cocoa, chocolate, or other preparations of the nuts of *Theobroma cacao*, if only honestly made, have a very high nutritive value. But several authorities here quoted show that of the total nitrogen present a very considerable part occurs in the forms of theobromine, ammonia (!), amido-compounds, and other indigestible nitrogenous substances; so that from 30 to 40 per cent of the total nitrogen is not in an assimilable state. For the details, and for the names of the authorities cited, we must refer to the work before us.

The frauds committed upon the public in the sale of coffee and tea are now much less rampant than formerly. But far too much remains. It is a humiliating fact that whilst we pass Acts concerning the sale of food and drugs, and appoint public analysts, we actually grant patents for new methods of adulteration, or rather for making up rubbish into the shape of coffee-beans.

Some reference is made by Mr. Allen to such patents. But so long as the libel laws—"the shield and the sword of the quack and the swindler"—remain rampant, it is impossible to speak truthfully of such proceedings.

One important step would be an enactment that if any substance is made or vended as an addition to coffee or tea, or if the words coffee or tea are used in its name or description, it shall fall within the scope of the Sale of Food and Drugs Act. At present such compositions as "French Coffee," "Coffee as in France," &c., pass free!

Fraudulent coffee-beans are not unknown in Germany, where they are sold as Kunst-Kaffee, Domkaffee, Allerweltkaffee, Mogdad Kaffee, &c. But in that country they do not enjoy the protection of patents.

The absolute identity of theine and caffeine, though generally assumed, is here spoken of as not established beyond doubt.

In treating of the toxicology of opium and its allies, the author exposes some of the exaggerations of the "anti-opiumists." These denounced drugs seem to be almost a necessity of life in malarious districts, not merely in India and China, but in the fenny parts of England. The agitator would do well to note the quantity of laudanum made up and sold every market-day at Horn-castle. It is interesting to observe that so-called "paregoric" is now sold by costermongers! The author remarks that these concoctions, if harmless in themselves, accustom ignorant persons to deal with preparations of opium, and if by any chance genuine paregoric falls into their hands, there is no small danger of an overdose. But the costermonger is, perhaps, as well qualified to dispense poisonous medicines as the draper or the grocer.

The permanence of strychnine in dead bodies even for years is emphasized,—a subject which reminds us of one of the least satisfactory features of the Palmer case.

Strychnine is pronounced, on the authority of Dr. Müller, of Yackandandah, Victoria, to be a good antidote in snake-bite. Among one hundred cases thus treated hypodermically all save one recovered. The species of snake is not mentioned. The question is, would it prove successful against the poison of the cobra?

We can only say, in concluding our brief notice of this admirable work, that it will be found necessary in every laboratory.

Metal Colouring and Bronzing. By ARTHUR H. HIORNS, Principal, Metallurgy and Engineering Department, Birmingham Municipal Technical School. London and New York: Macmillan and Co., 1892. 8vo., pp. 336.

It is exceedingly satisfactory to perceive that a number of technical manuals are now making their appearance which are not mere compilations of recipes strung together at hap-hazard by a compiler innocent of practical knowledge. Mr. Hiorns, on the contrary, though he has diligently collected information on his subject from all available sources, has submitted all recipes obtained to a careful experimental investigation with which he and his colleagues have been engaged for eighteen months. In his preface he calls attention to the nicety of the conditions on which success or failure may turn. The manipulation may in some cases be defective as well as the reagent. Though not exactly in the same words, he recommends his pupils and readers to "mix their colours with brains."

The work emanates from the Birmingham Municipal Technical School,—a most praiseworthy Institution. It appears that the art of producing beautiful colours on metal work had formerly one of its chief centres in Birmingham. It is now, we regret to see, spoken of as an "almost lost art," and we most heartily sympathise with the attempt of the Committee of the School and with Mr. Hiorns not merely to bring it back but to elevate and extend it.

We find with pleasure that the author duly regards

metal colouring as a chemical art, which, if it is to rise above "rule of thumb," pre-supposes a knowledge of chemical principles. These principles, together with the preliminary treatment of metallic objects, form the subject of the first two parts. The remainder of the work is devoted to the three main kinds of colouring, viz., chemical metal colouring, electro-chemical metal colouring, and mechanical metal colouring. For his instructions we must refer the reader to the work itself, expressing our hope that Mr. Hiorns' labours may be duly appreciated and may contribute towards the truly patriotic object which he has in view.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 17, October 24, 1892.

New Researches on the Fixation of Atmospheric Nitrogen by Microbia.—M. Berthelot.—The author's experiments show that no fixation of atmospheric nitrogen by the mere fact of a purely chemical oxidation of the humic acid is effected by the simultaneous action of air and light. But the humic acid serves as a necessary support for the microbia, and in its absence they cannot effect the fixation of the nitrogen.

Protection from Rabies.—The Perpetual Secretary communicated a letter from the French Association for the Advancement of Science in which two prizes of 400 and 200 francs respectively are offered for the best study of the following question: The frequency of rabies and the prophylactic measures in force in any one department (except La Seine), or in a region of two or three departments in France and Algeria. The statistics must extend over at least ten years, and must include the results of 1892.

The Dissociation of Chrome Alum.—H. Baubigny and E. Péchard.—The dissociation of numerous saline compounds on solution is now a well-established fact. At times the formation of a less soluble compound, e.g., a sub-salt or a change of colour, render the occurrence of such a dissociation perceptible. Often it is more difficult to characterise. Graham, by availing himself of the different rates of the diffusion of potassium sulphate and aluminium sulphate, has been able to demonstrate this fact in the case of ordinary alum. On placing a solution of this salt at the bottom of a vessel full of water, he observed, after some time, on analysing the upper stratum of liquid, that the weights of the two sulphates did not co-exist in the proportions corresponding to the production of alum. But as everything becomes equalised in course of time, the phenomenon of dissociation can be studied by this procedure only in the first portion of time. This fact of dissociation may be demonstrated in the chrome-alums in a more distinct manner. Having remarked that ordinary chrome-alum, after being repeatedly precipitated from its aqueous solutions by means of alcohol, always presented an acid reaction, we added to 20 c.c. of a saturated solution 300 mgrms. of ammoniacal gas; after stirring, it was neutral to methyl-orange. Some time afterwards the solution, which had taken a green colour on the addition of ammonia, deposited violet crystals of a distinctly acid reaction, and the mother liquors also became again acid to methyl-orange. This fact can only depend on a partial decomposition of the salt, corresponding to such a state of equilibrium that the liquid is finally acid. This peculiarity is due to the chromium sulphate, for on repeating the experiment with this simple sulphate we found with this compound a

perfectly analogous phenomenon. Ordinary alum and aluminium sulphate do not display the same property. Their solutions, if neutral to methyl-orange, remain at the end of eight days.

Temperature of the Maximum Density of Aqueous Solutions.—L. de Coppel.—There exists an interesting relation between the fall of the congelation-point (C) and the fall of the temperature of maximum density (D). All the substances hitherto studied (except alcohol, and possibly sulphuric acid), are divisible into three groups

with reference to the value of the proportion $\frac{D}{C}$. The first group consists of substances which reduce the temperature of the maximum density of water about four times more than they reduce its congelation-point. This group comprises at present caustic potassa, oxalic acid, sodium, potassium and calcium chlorides, and potassium iodide. A second group comprises substances which, like sugar and the alkaline carbonates and sulphates, lower the temperature of the maximum density seven or eight times more than the temperature of congelation. In the third group, which at present is represented only by copper sulphate, the proportion between the two reductions is about eleven or twelve. We see that the three values of the relation $\frac{D}{C}$ are to each other approximately as 1:2:3.

Thermic Value of the Three Functions of Orthophosphoric Acid and on its Constitution.—M. de Forcrand.—This memoir does not admit of useful abstraction, and is not of sufficient importance for insertion in full.

The Preparation and Properties of Fibroine.—Leo Vignon.—Raw silk consists of two portions separable by means of different reagents. Industrially this is effected by means of boiling soap-lye, the result being 25 parts of the so-called gum and 75 parts of true silk. Mülder removed the gum by the action of boiling acetic acid, and obtained from 53 to 54 parts of fibroine or true silk, and from 46 to 47 parts of soluble matter including the gum. Staedler treated raw silk for eighteen hours in the cold with a 5 per cent lye of soda. He obtained from 42 to 50 per cent of a substance which he considered as pure fibroine. Cramer used water under pressure at 133° and obtained fibroine equal to 66 per cent of the silk. Francezau adds upon raw silk with two boiling soap-baths and two successive baths of acetic acid at 8°. He obtains as a mean 75 per cent of fibroine. The author treats with two successive baths of neutral white soap (150 grms. soap to 1500 c.c. of distilled water), respectively, for thirty to twenty minutes. After the first bath the skeins are rinsed in distilled water, first hot and then luke-warm. After the second soaping the silk is rinsed with boiling distilled water, with luke-warm distilled water, with cold distilled water containing per litre 10 c.c. of pure hydrochloric acid at 22°. Lastly, it was rinsed once with distilled water, and twice with alcohol at 90°. The yield is 75 per cent of a very white, brilliant, supple, tenacious and elastic material, which the author regards as fibroine. Its specific gravity is 1.34. Its centesimal composition is—Carbon 48.3; hydrogen 6.5; nitrogen 19.2; oxygen 26. It contains only 0.01 per cent of mineral matter. If dissolved in concentrated hydrochloric acid it acts upon polarised light and is strongly lævo-rotatory.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. July, 1892.

This issue gives an account of the general Session held on May 27th for the distribution of prizes and medals. The Grand Prize of 12,000 francs, founded by the Marquis d'Argenteuil for the discovery of the greatest utility to French industry, was awarded to M. Berthelot, who is represented as the originator of organic synthesis.

August, 1892.

Report made by M. Troost, on Behalf of the Committee of the Chemical Arts, on the Automatic Manufacture of Vinegar, by E. Barbe.—This invention, which cannot be described without the accompaniment of the two large figures, dispenses with manual labour, the vats being fed mechanically with the utmost regularity by day and night.

MEETINGS FOR THE WEEK.

WEDNESDAY, 16th.—Society of Arts, 8. Opening Address of the 139th Session by Sir Richard E. Webster, Q.C.

THURSDAY, 17th.—Chemical, 8. "Fluosulphonic Acid," by Prof. Thorpe, F.R.S., and William Kirman, A.R.C.S. "The Interaction of Iodine and Potassium Chlorate," by Prof. Thorpe and George H. Perry, A.R.C.S. "Magnetic Rotation of Sulphuric and Nitric Acids and their Solutions, also of Solutions of Sodium Sulphate and Lithium Nitrate," by W. H. Perkin, F.R.S. "Note on the Refractive Indices and Magnetic Rotation of Sulphuric Acid Solutions," and "Hydrates of Alkylamines," by S. U. Pickering, F.R.S. "The Atomic Weight of Boron," by Prof. Ramsay, F.R.S., and Miss Emily Aston. Other papers.

ERRATUM.—P. 223, col. 1, line 10 from bottom, for "MS," read—
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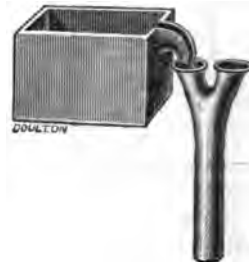


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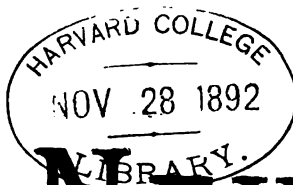
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Edited by **Wm. Crookes, F.R.S.** (WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE") [Established **Forty-Eight Years.**]

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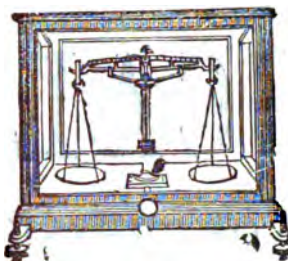
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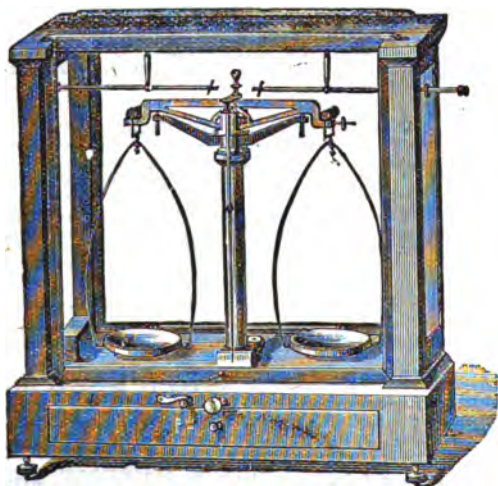


FIG. 34.

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THE CHEMICAL NEWS.

VOL. LXVI., No. 1721.

THE CONFIGURATION OF GRAPE-SUGAR AND ITS ISOMERS.*

By W. E. STONE, Purdue University.

THE researches of Emil Fischer upon the constitution and synthesis of sugars are well known through his numerous papers in the *Berichte*. The same have been reviewed in the *American Chemical Journal* (xi., 277, and xii., 357), and also in *Agricultural Science* (vi., No. 4). These researches have now proceeded so far, and the results harmonise so entirely with the theory of the asymmetric carbon atom, that Fischer proposes in two late papers (*Ber. Deut. Chem. Gesell.*, xxiv., 1836 and 2683), to assign certain specific configurations to those of the sugars which have been well studied.

Bold as this undertaking seems, his conclusions, all based on experimental data, conform to the requirements of the theory and are ingeniously and skilfully drawn.

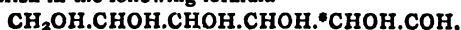
According to the theory there may exist sixteen isomers of the structure of grape-sugar, and for those derivatives of the same which have symmetrical molecules, i.e., dibasic acids and hexavalent alcohols, ten different structures are possible. These structures are expressed by the following table taken from van't Hoff-Herrmann's paper, "Die Lagerung der Atome im Raume," in which the signs + or - are used to indicate the relative arrangement of the hydrogen and hydroxyl upon the four non-terminal carbon atoms of the sugar molecule, accordingly as their sequence conforms to the direction in which the hands of a watch move, or the reverse.

				11	12	13	14	15	16
				+	+	+	+	+	-
				+	+	+	-	-	+
				+	-	-	+	-	-
				-	+	-	-	-	-
+	+	-	-	-	+	-	-	-	-
+	-	+	-	+	-	-	+	-	-
+	-	+	+	+	+	+	-	+	+
+	+	-	+	+	+	+	+	+	-
1	2	3	4	5	6	7	8	9	10

Of these it is evident that the arrangements 5-10 are identical with 11-16, so far as the alcohols or dibasic acids are concerned.

In order now to assign one of these configurations to grape-sugar upon the ground of experimental data it is necessary to consider the saccharic acid of which both optical forms are known. The d. saccharic acid is derived from both the d. and l. glucose (*Ber.*, xxiv., 521), they being stereoisomeric. Hence the two acids must be included in cases 5-10, since only such can be derived from stereoisomeric sugars. But of these numbers, 7 and 8 are optically inactive and therefore not to be considered. Of the remaining cases numbers 6 and 10 may also be rejected on the ground of the following experimental proofs.

Glucose and mannose differ from each other only in the configuration of the carbon atom, designated by an asterisk in the following formula—



and the same, of course, holds true for their derivatives (sorbite and mannite, gluconic and mannonic acids, and saccharic and manno-saccharic acids). The proofs of this hypothesis are strong as presented by Fischer:—

* From the *American Chemical Journal*, xiv., No. 5.

1. Mannose and glucose yield the same "osazon" (*Ber.*, xxii., 374).

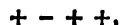
2. Arabinose, by the addition of hydrocyanic acid, HCN, yields in the same reaction l. mannonic and l. gluconic acids (*Ber.*, xxiii., 2611).

3. Fructose is reduced by sodium-amalgam to a mixture of mannite and sorbite (*Ber.*, xxiii., 3684).

4. Mannonic and gluconic acids, on being heated with pyridine or quinoline, are each transformed into the other (*Ber.*, xxiii., 800).

5. All attempts to separate mannonic or gluconic acids into different components have failed (*Ber.*, xxiii., 800).

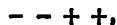
Accepting these proofs of the relative structure of the above bodies, numbers 6 and 10 become impossible, for the following reasons. If saccharic acid, or what is the same thing, sorbite, had the structure 6—



or 10—



then the manno-saccharic acid or the mannite would have the structures 7—



or 8—



but these are both inactive combinations, while the mannite and manno-saccharic acid are both active.

There remain, therefore, for the d. and l. saccharic acids only the two configurations 5 and 9, and since it is immaterial just which arrangement of hydrogen and hydroxyl one understands by + and which by -, Fischer assigns arbitrarily the configuration 5 to d. saccharic acid—



and 9 to the l. saccharic acid—



But corresponding to the d. saccharic acid are two aldehyd sugars, d. glucose, or grape-sugar, and the d. gulose, a synthetic product. These, being stereoisomeric, would have the configurations—

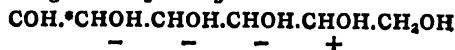


and



In order to assign one of these definitely to grape-sugar and the other to d. gulose, it is necessary to again extend our observations to another series of sugars, viz., the pentoses.

From one of these, arabinose, is derived l. glucose, and from the other (*Ber.*, xxiv., 529), xylose, comes l. gulose. For these latter (l. glucose and l. gulose) there remain the configurations 9 and 15—



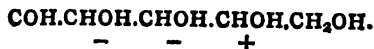
and



In these formulæ the asymmetric carbon atoms designated by the asterisk have been created by synthesis and do not exist in arabinose and xylose. Rejecting them, we have as the possible configurations of the two pentoses—

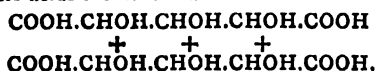


and

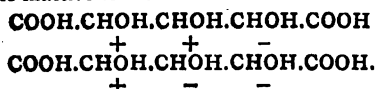


For the pentoses of the structure of arabinose and xylose (aldehyds) there are eight possible isomers, or for

the corresponding dibasic acids or alcohols the number is four, of which two are active and two inactive systems. The theoretical configurations of the two active forms of the dibasic acids are as follows:—



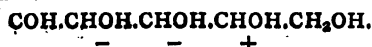
and of the inactive forms—



The optical behaviour of the acids or alcohols derived from arabinose and xylose would therefore serve to indicate in which of the above couples their configuration belongs. Here again the experimental testimony is clear, for both the arabite (upon the addition of borax) and the trioxo-glutaric acid from arabinose showed *lævo*-rotation. Arabinose, therefore, belongs to one of the two active systems, preferably the second, and its configuration would be as follows:—



The xylose, on the other hand, belongs to the inactive systems, since the xylite, even with borax, and the trioxo-glutaric acid from xylose, are both without influence upon polarised light. To the xylose therefore is assigned this configuration—



The configurations thus experimentally indicated for these sugars would of course hold for their derivatives among the hexoses, viz., the *l.* glucose and *l.* gulose, and from these the configurations of other members of the group are easily deduced, as follows:—

Hexose Sugars.

Aldoses.	COH	CHOH	CHOH	CHOH	CH ₂ OH
<i>d.</i> glucose,	—	+	+	+	—
<i>l.</i> glucose,	+	—	—	—	—
<i>d.</i> gulose,	+	+	+	—	—
<i>l.</i> gulose,	—	—	—	+	+
<i>d.</i> mannose,	+	+	+	+	+
<i>l.</i> mannose,	—	—	—	—	—

(For galactose the experimental data do not yet justify a choice between the four possible configurations indicated by a study of the mucic and allomucic acids.)

Ketoses.	COH	CO	CHOH	CHOH	CH ₂ OH
<i>d.</i> fructose,	—	+	+	+	—
<i>l.</i> fructose,	+	—	—	—	—

The mono- and dibasic acids and hexavalent alcohols derived from these sugars retain their respective configurations, and we have therefore reasonable experimental proof of the configuration of upwards of twenty bodies which are either sugars or closely related to them.

Fischer takes good care to remark, however, that these conclusions can only stand provided the theory of the asymmetric carbon atom is wholly in accord with the facts, and provided the oxidation of arabinose and xylose to the respective trioxo-glutaric acids occurs without intramolecular changes.

In the expressions used above, however, the signs + and — may easily be misinterpreted, and to prevent confusion, Fischer in a second paper presents these configurations in a clearer manner. Taking the familiar models of the carbon atoms, and constructing the sugar molecules according to the configurations proposed above, he develops graphic formulæ which have a new significance and permit an easy comparison of the different sugar molecules,

The four asymmetric carbon atoms may be designated by numbers, as follows—

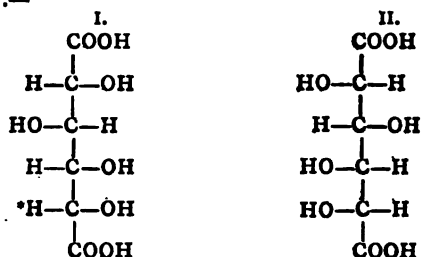


In the discussion of van't Hoff, upon which Fischer's deductions are based, the carbon atom 1 is compared only with 4, and 2 with 3. Consequently, in the configuration assigned to *d.* glucose or grape-sugar,—

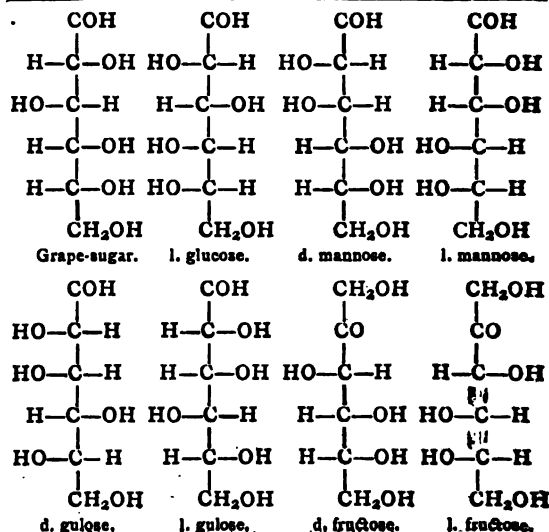


the arrangement of hydrogen and hydroxyl upon 1 is the opposite of that upon 4, while 2 and 3 are alike. If 1 be compared with 3 it is found that the arrangement is also the same. From a superficial examination the same would seem to follow for 1 and 2, but this is not the case, for the sign of 2 changes accordingly as it is compared with 3 or 1, as is apparent from the study of the model.

That is, the above expression for the configuration of grape-sugar permits of two interpretations, and to avoid confusion the structure is represented graphically as follows. By means of the flexible rubber models the molecules of the *d.* and *l.* saccharic acids are constructed; these are then placed upon a plane surface in such way that the carbon atoms lie in a straight line, when the hydrogens and hydroxyls arrange themselves on either side, and by projection present the following arrangements:—



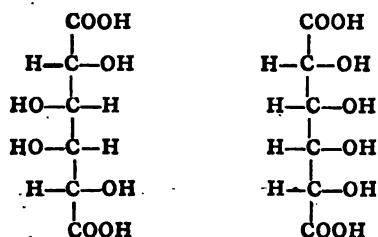
The same appearance is also obtained by the use of the inflexible wire models, arranging the carbon atoms in a vertical plane and regarding the structure from above. Fischer selects the first from the two above expressions for the *d.* saccharic acid, whereby it is again immaterial if, at starting, the arrangement of hydrogen and hydroxyl upon the starred carbon atom does or does



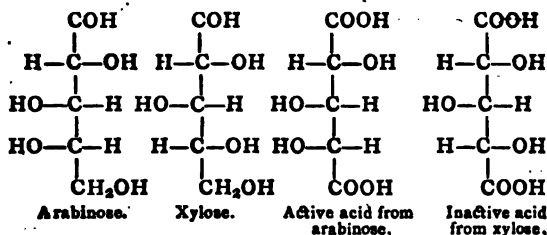
not follow the motion of the hands of a watch. From this, therefore, are derived the accompanying graphic representations of the configurations of the d. glucose and its isomers, the same being projections of models constructed on the basis of the configurations already indicated by the + or - signs. (See preceding column).

Of course these projection formulæ have a quite different significance from others of similar appearance which have been proposed before.

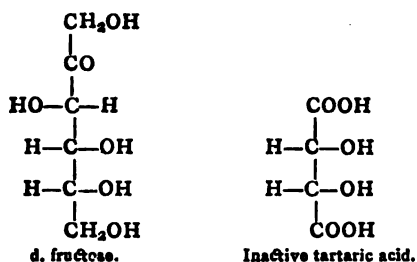
The projections for the two inactive dibasic acids of the dulcitol series, which probably exist as the mucic and allomucic acids, are also given, as possibly furnishing some insight into the configuration of the galactose.



In the same way the following projections for the pentoses and their corresponding trioxo-glutaric acids are obtained:—



Working from these formulæ, the models of the molecules are easily constructed in which the + or - arrangement of each asymmetric carbon atom is readily seen. Their value is also apparent in the study of such reactions as increase or decrease the number of asymmetric carbon atoms, as an example of which the oxidation of fruit-sugar or levulose to inactive tartaric acid is given. The comparison of the projection formulæ of the two bodies renders it apparent how this reaction is possible.



Undoubtedly this insight thus obtained into the constitution and configuration of the sugars will point out the way to new reactions and to new explanations of known reactions; and in any event, Fischer's work, of which these last papers present the climax, constitutes the most notable contribution yet made to the subject.

Experiments on Bread and Biscuit.—M. Balland.—The author holds that the degree of hydration of bread depends much on the shape of the loaves. For equal weights a long loaf is preferable to one of a round form. —*Comptes Rendus*, cxv., No. 18.

SUCROSE, DEXTROSE, LEVULOSE: THEIR QUANTITATIVE DETERMINATION WHEN OCCURRING TOGETHER.*

By F. G. WIECHMANN, Ph.D.

(Concluded from p. 239).

Experimental Test of Method.

Instruments Employed.—The polariscope used was a half shade instrument of Scheibler's make; every degree of its scale had been tested with a control tube of Schmidt and Hänsch.

The polarisations were all made with a Schmidt and Hänsch water-jacketed tube 200 m.m. long. The temperature of the solutions was determined by a small Centigrade thermometer graduated in tenths of a degree, made by the above firm, and of Jena normal glass. All readings in the polariscope were made by two observers; the observations were generally made every half degree Centigrade, from 17° to 20° C., but of course only the values obtained at 20° C. were placed on record.

Materials Used in Experiments.—The sucrose, the dextrose, and the levulose used in the experiments were all prepared under the writer's direction.

The sucrose was made from the purest granulated sugar (polarisation 99.9–100.0) by repeated washing with absolute ethyl alcohol. A determination of the specific rotatory power of the sucrose in a 10 per cent solution (10.0 grms. dry substance in 100 c.c.) gave $[\alpha]_D^{20} = +66.5$.

The dextrose was prepared from commercial anhydrous dextrose by treatment with best blood carbon and by repeated crystallisation from absolute ethyl alcohol.

A determination of the specific rotatory power of the dextrose in a 10 per cent solution (10.0 grms. dry substance in 100 c.c.) gave $[\alpha]_D^{20} = +53.5$.

A determination of the reducing power of this material made by the method of J. Allihn, showed that 0.250 grm. dry substance of the dextrose reduced of metallic copper—

Determination 1 = 0.4655 grm.

Determination 2 = 0.4663 „

In Allihn's table 0.2499 grm. of dextrose corresponds to 0.4630 grm. Cu.

The levulose was prepared essentially according to the method of H. Ost (*Zeitschrift für Analytische Chemie*, 1890, p. 648) from inuline, prepared by H. Trommsdorff, of Erfurt. 100.0 grms. of inuline, 250.0 grms. of water, and 1.226 grms. of hydrochloric acid (specific gravity 1.20) were used. About three months after the work was commenced, and after being twice crystallised from absolute ethyl alcohol, the levulose obtained was tested.

Duplicate determinations of the specific rotatory power of this specimen were made with all possible care, and it was found that in a 10 per cent solution (10.0 grms. dry substance in 100 c.c.) the value of $[\alpha]_D^{20} = -81.9$.

A determination of the reducing power of this material on copper solution was made by Allihn's method for dextrose, exactly as quoted by Hönl and Jesser (*Zeitschrift des Vereines für Rübensucker-industrie*, 1888, vol. xxxviii., p. 1035), and this showed that 0.250 grm. of dry substance reduced of metallic copper—

Determination No. 1 = 0.4319 grm.

Determination No. 2 = 0.4309 „

Referring to Hönl and Jesser's investigation it will be seen that they found 0.250 grm. of pure levulose reduced 0.428 Cu.

The $[\alpha]_D^{20}$ value of this sample of levulose – 81.9 is identical with that quoted by Tollens (*Kurzes Handbuch der Kohlenhydrate*, p. 86) as obtained by calculation from data furnished by Dubrunfaut, Lescœur, and Morelle.

As the values for $[\alpha]_D^{20}$ found by Tollens and others differ greatly from this figure – 81.9 as well as from each other, there seems urgent need of an investigation to

* From the *School of Mines Quarterly*, xiii., No. 3.

Series I.

Experiment.	1.*			2.*			3.*		
	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.
Polarisation in circular degrees	-0.0033	0.0000	+0.0033	-1.3870	-1.3728	-0.0142	-0.7100	-0.7036	-0.0064
Dextrose	3.00	3.02	+0.02	2.00	2.01	+0.01	2.50	2.51	+0.01
Levulose	2.00	1.98	-0.02	3.00	2.99	-0.01	2.50	2.49	-0.01

Series II.

Experiment.	1.			2.*			3.*			4.		
	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.
Polarisation in circular degrees	6.2465	6.2909	+0.0444	6.1788	6.1744	-0.0044	6.3142	6.2909	-0.0233	6.1918	6.2576	+0.0658
Sucrose	9.50	—	—	9.50	—	—	9.50	—	—	9.60	—	—
Dextrose	0.25	0.283	+0.033	0.20	0.197	-0.003	0.30	0.283	-0.017	0.10	0.149	+0.049
Levulose	0.25	0.217	-0.033	0.30	0.303	+0.003	0.20	0.217	+0.017	0.30	0.251	-0.049

Series III.

Experiment.	1.			2.*			3.*			4.*		
	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.
Polarisation in circular degrees	5.4395	5.3922	-0.0473	5.2364	5.2424	+0.0060	5.6426	5.6418	-0.0008	5.0463	5.0427	-0.0036
Sucrose	8.50	—	—	8.50	—	—	8.50	—	—	8.60	—	—
Dextrose	0.75	0.715	-0.035	0.60	0.605	+0.005	0.90	0.900	0.000	0.35	0.347	-0.003
Levulose	0.75	0.785	+0.035	0.90	0.895	-0.005	0.60	0.600	0.000	1.05	1.053	+0.003

Series IV.

Experiment.	1.			2.*			3.*			4.		
	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.
Polarisation in circular degrees	4.6325	4.5934	-0.0391	4.2940	4.2938	-0.0002	4.9710	4.9928	+0.0218	3.9008	3.8611	-0.0387
Sucrose	7.50	—	—	7.50	—	—	7.50	—	—	7.60	—	—
Dextrose	1.25	1.221	-0.029	1.00	1.000	0.000	1.50	1.517	+0.017	0.60	0.571	-0.029
Levulose	1.25	1.279	+0.029	1.50	1.500	0.000	1.00	0.983	-0.017	1.80	1.829	+0.029

Series V.

Experiment.	1.*			2.*			3.*			4.		
	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.
Polarisation in circular degrees	3.8255	3.7945	-0.0305	3.3516	3.3285	-0.0231	4.2994	4.3271	+0.0277	2.7553	2.7127	-0.0426
Sucrose	6.50	—	—	6.50	—	—	6.50	—	—	6.60	—	—
Dextrose	1.75	1.728	-0.022	1.40	1.383	-0.017	2.10	2.121	+0.021	0.85	0.819	-0.031
Levulose	1.75	1.772	+0.022	2.10	2.117	+0.017	1.40	1.379	-0.021	2.55	2.581	+0.031

determine whether the specific rotatory power of levulose varies according to the source from which it is prepared, according to the method of its preparation, or possibly according to both.

In these experiments, of course, the value of l in the formula for calculating the results of the analyses has been placed equal to -0.819 .

Record of Experiments.—In all, five series of tests were made. In the first series, dextrose and levulose only were used in order to study the behaviour of these two sugars in the absence of sucrose and when mixed in different proportions. In the remaining four series, sucrose, dextrose, and levulose were employed in varying proportions.

All polarisations were made on 10 per cent solutions (10.000 grms. dry substance in 100 c.c.) at the temperature of 20°C . All polarisations were made, as before stated, in a sugar polariscope, and transformed into circular degrees by multiplying with 0.346 .

The reliability of the gravimetric methods of determining the sucrose and the total reducing sugars having been amply demonstrated by a great number of experiments made at an earlier date, it was not deemed necessary to execute them in this work, and therefore the amounts of sucrose and of the total reducing sugars used in making the solutions are assumed as having been determined by analysis.

To correctly appreciate the meaning of the results here recorded, it must be remembered that 1° on the scale of

the sugar polariscope in these observations is equal to 0.346 circular degree. One-tenth of a degree on the sugar scale therefore corresponds to 0.0346 of a circular degree.

It will be granted that it is impossible to make an observation on a sugar scale which shall approximate closer to the truth than ± 0.1 of a degree. As this is equal to 0.0346 circular degree it will be but fair to regard all those observations made on the polariscope which come within these limits, viz., ± 0.0346 of a circular degree, as theoretically correct.

Making this allowance, inspection of the nineteen observations recorded in Series I. to V. inclusive show that of this number only six do not agree with the theoretical values. These exceptions are here given, and they exceed the limit of ± 0.0346 of a circular degree but slightly.

Series.	No.	Amount of difference.
II.	1	0.0098
II.	4	0.0312
III.	1	0.0127
IV.	1	0.0045
IV.	4	0.0041
V.	4	0.0080

Five of these determinations are but very little outside of the limits assumed, and even the poorest of them all, Series II., No. 4, would come well within the limits if ± 0.2 of a degree of the sugar polariscope be adopted as

the range of variation in the readings. With a more finely graduated instrument much closer readings could of course be made.

The Tables as given, however, show the amounts of levulose and of dextrose calculated from the polarisations *actually obtained* and without making any allowance whatsoever.

All experiments marked with a star would have yielded the results theoretically required, that is to say, absolutely correct values, provided that ± 0.1 of a degree on the sugar polariscope had been allowed for variation in the readings; and if a range of ± 0.2 of a degree on the sugar polariscope had been allowed in taking the readings, *all experiments without exception* would have shown the analysis to have determined the amounts theoretically required.

For exact scientific investigations, for instance, for accurately determining the kind and amounts of these three sugars in sugar-producing plants at different stages of their growth, &c., a delicate and finely graduated polariscope is required, but the work here recorded bears ample evidence of the fact that this method can be employed to advantage with the facilities provided for in every well equipped sugar laboratory.

THE REICHERT PROCESS FOR BUTTER, &c.

By H. DROOP RICHMOND.

IN the CHEMICAL NEWS, vol. lxxvi, p. 199, Mr. J. A. Wilson contributes a paper under the above title; he states that exact agreement between two operators will not be possible, unless the same quantities of the same acid and alkali are used by each.

Mr. Wilson evidently argues from analogy between acetic and butyric acids, his experiments (*Journ. Soc. Chem. Ind., ix., No. 1, misprinted x. in original*) having shown that the rate of distillation of acetic acid is affected by the presence of various salts in the solution distilled. He also states that this point has occupied notice; I cannot help thinking that "occupied" is a misprint for "escaped."

I may point out that Mansfeld, who uses caustic potash for saponification, states that his results are the same as those obtained by Wollny's (misprinted Woolny in Mr. Wilson's paper) method, and other experimenters have shown that the two agree within the limits of experimental error. In the *Stazioni Sperimentali Agrarie Italiane*, xxiii., No. 1., I have shown that butyric acid distills according to the following formula:—

$$y = 2.22x - 0.0151x^2 + 0.000031x^3.$$

x = quantity of distillate from 100 parts, and y = percentage of butyric acid distilled.

From this I calculate that when distilling 50 c.c. out of 75 c.c., 89.1 per cent should pass over, and when distilling 110 c.c. out of 140 c.c., 96.3 per cent should pass over. Actual experiment gave me 89.6 per cent and 96.9 per cent respectively when the quantities of acid and alkali used in the Reichert and Reichert-Wollny methods were added, and 89.7 per cent and 97.2 per cent when in addition 2.2 and 4.4 grms. of fatty acids were added.

I have also made a series of experiments, using Leffmann and Beam's modification, i.e., the use of glycerin for saponification in place of alcohol, and find a very slight increase in the quantity distilled, amounting on an average to 0.7 per cent.

I think that a reasonable variation of the amount of salts or other substances tending to raise the boiling-point will not affect the results within the limits of experimental error.

Mr. Wilson has pushed the case of analogy too far; in his paper before referred to, he quotes Duclaux's researches, but in the last one he has not borne them

sufficiently in mind. Duclaux shows that the volatility of the homologous fatty acids soluble in water increases with their molecular weight; thus, while under the conditions of the Wollny process, acetic acid furnishes less than 60 per cent in the distillate, butyric acid gives 96 per cent, and the higher acids more; there is not room for much variation when so high a percentage as 96 per cent is distilled. In Mr. Wilson's experiments on acetic acid, the distillation was pushed much further than in the Wollny process; allowing 2 c.c. for the vapour in flask and condenser, he had but 7 per cent left, while in the Wollny process there is 11.4 per cent, and the concentration of the salts, and consequently boiling-point, is much less in the latter; it is in the highest degree probable that the excess found by Mr. Wilson, when salts were present, distilled over chiefly in the latter stages of the distillation.

Of course in an accurate scientific investigation the point raised by Mr. Wilson could not be neglected, but in an analytical method where the experimental error is 2 or 3 per cent, theory suggests and practice confirms that it is negligible.

50, Clanricarde Gardens, Baywater, W.,
October 22, 1892.

REPORT ON POTASH.*

By Dr. GEORGE F. PAYNE, Atlanta, Ga.,
State Chemist of Georgia

THE work required by the Association of the reporter on potash for 1892 was an investigation as to whether the use of sodium chloride was essential in the Lindo-Gladding method of determining potash)

Four samples were prepared and were numbered one, two, three, and four.

Number one was a high grade sulphate of potash.

Number two was an acid phosphate with sulphate of potash in the form of kainit.

Number three was an acid phosphate with sulphate of potash in the form of kainit, and containing 5 per cent of double sulphate of alumina and ammonia.

Number four was identical with number three, with the substitution of 5 per cent of soluble sodium silicate in place of the double salt of alumina and ammonia.

The ingredients of each sample were first finely powdered and thoroughly mixed, then sifted through a very fine sieve, then again intimately mixed, and portions taken from forty different parts of the pile were well remixed and used for filling the bottles. Only the best xx superfine long taper corks were used, and were selected long enough to project well from the mouth of the vial to secure easy opening and air-tight re-corking. The corks were all well sealed with paraffin. With each package a circular was sent requesting that the determinations be made as soon as convenient after receiving samples to eliminate as far as possible any differences likely to occur from changes in the amount of moisture after bottling.

Each chemist was also requested to carry out the method as ordinarily managed in his laboratory, working each sample with and without sodium chloride, side by side, and as nearly as possible under exactly the same conditions.

Twenty-two chemists took part in the work, and their results are given in the Table.

Notes from Correspondents.

NORMAN ROBINSON, Florida.—As to the addition of NaCl, I have long since discarded it in regular laboratory work, as I never was able to satisfy myself that it was of enough benefit to pay for the additional expense in platinic chloride.

* For the Association of Official Agricultural Chemists of the United States.

Determination of Potash by the Lindo-Gladding Method with and without Sodium Chloride.

Names of Analysts and Location. Official Laboratories.	Sample No. 1.		Sample No. 2.		Sample No. 3.		Sample No. 4.	
	With NaCl.	Without NaCl.	With NaCl.	Without NaCl.	With NaCl.	Without NaCl.	With NaCl.	Without NaCl.
Norman Robinson, State Chemist, Tallahassee, Florida	48'83	48'70	1'58	1'59	1'47	1'46	1'40	1'41
F. S. Shiver, Assistant of State Chemist, Fort Hill, South Carolina (a) .. .	49'05	49'13	1'45	1'44	1'40	1'39	1'40	1'44
F. S. Shiver, Assistant of State Chemist, Fort Hill, South Carolina (b) .. .	49'00	—	1'45	—	1'40	—	1'32	—
P. L. Hutchinson, Assistant of State Chemist, Atlanta, Georgia .. .	49'05	49'15	1'50	1'48	1'51	1'40	1'48	1'40
J. F. Wilkinson, Assistant of State Chemist, Atlanta, Georgia .. .	49'13	49'12	1'50	1'52	1'47	1'42	1'36	1'34
F. B. Carpenter, Experiment Station, Raleigh, North Carolina .. .	48'94	—	1'61	—	1'48	—	1'56	—
Thos. L. Blalock, Experiment Station, Raleigh, North Carolina (a) .. .	48'76	48'76	1'63	1'63	1'48	1'46	1'48	1'47
Thos. L. Blalock, Experiment Station, Raleigh, North Carolina (b) .. .	48'96	49'10	—	—	—	—	—	—
Thos. L. Blalock, Experiment Station, Raleigh, North Carolina (c) .. .	48'90	48'91	1'59	1'58	1'51	1'48	1'46	1'45
Louis A. Voorhees, Experiment Station, New Brunswick, New Jersey .. .	49'23	49'19	1'49	1'46	1'35	1'36	1'36	1'37
Louis A. Voorhees, Experiment Station, New Brunswick, New Jersey .. .	49'27	49'29	1'51	1'52	1'38	1'42	1'36	1'37
Chas. S. Cathcart, Agricultural College, New Brunswick, New Jersey .. .	49'31	49'34	1'52	1'46	1'43	1'45	1'35	1'33
E. H. Farrington, Experiment Station, Champaign, Illinois .. .	49'29	49'00	1'77	1'64	1'77	1'66	1'62	1'51
Thos. L. Watson, Experiment Station, Blacksburg, Virginia, Assistant Chemist .. .	49'19	48'95	1'55	1'58	1'41	1'42	1'41	1'36
R. C. Kedzie, Agricultural College, P. O., Michigan .. .	48'75	48'69	1'55	1'53	1'54	1'51	1'67	1'65
Rudolf de Roode, Experiment Station, Morgantown, West Virginia .. .	48'96	48'96	1'52	1'55	1'42	1'42	1'37	1'39
Rudolf de Roode, Experiment Station, Morgantown, West Virginia .. .	49'04	49'04	1'57	1'53	1'48	1'46	1'39	1'37
C. B. Collingwood, Experiment Station, Tucson, Arizona .. .	48'62	48'38	1'51	1'47	—	—	—	—
Henry E. Curtis, Experiment Station, Lexington, Kentucky .. .	49'00	48'91	1'45	1'46	1'43	1'40	1'39	1'37
W. S. Sweetser, Experiment Station, State College, P. O., Pennsylvania .. .	49'26	49'28	1'69	1'57	1'58	1'53	1'45	1'43
W. S. Sweetser, Experiment Station, State College, P. O., Pennsylvania .. .	49'30	49'29	1'62	1'57	1'51	1'51	1'45	1'40
H. B. McDonnell, State Chemist, College Park, P. O., Maryland .. .	48'47	48'69	1'65	1'61	1'58	1'55	1'48	1'45
W. D. Bigelow, U.S. Department of Agriculture, Washington, D. C. .. .	48'56	48'31	1'49	1'58	1'57	1'37	1'47	1'42
Average .. .	48'994	48'961	1'554	1'538	1'484	1'456	1'439	1'417
Difference .. .	—	0'033	—	0'016	—	0'028	—	0'022
Unofficial Laboratories.								
Shepard Laboratory, Charleston, South Carolina .. .	49'88	49'80	1'87	1'91	1'75	1'74	1'66	1'55
Elwyn Waller, School of Mines, Columbia College, New York City .. .	49'67	49'17	1'60	1'46	1'61	1'53	1'59	1'59
Elwyn Waller, School of Mines, Columbia College, New York City .. .	49'89	48'71	1'62	1'52	1'56	1'52	—	1'53
Elwyn Waller, School of Mines, Columbia College, New York City .. .	—	48'21	—	—	—	—	—	—
Elwyn Waller, School of Mines, Columbia College, New York City .. .	—	48'69	—	—	—	—	—	—
H. T. Vulte, Assistant of Elwyn Waller, School of Mines, Columbia College, N.Y. .. .	48'88	48'54	1'66	1'58	1'58	1'53	1'58	1'52
B. C. Hinman, Assistant of Elwyn Waller, School of Mines, Columbia College, N.Y. .. .	—	48'99	—	1'51	1'67	1'40	1'41	1'40
F. S. Hyde, Student of School of Mines, Columbia College, New York City .. .	49'43	49'47	1'35	1'42	—	—	—	—
Average .. .	49'550	48'948	1'620	1'566	1'634	1'544	1'560	1'518
Difference .. .	—	0'602	—	0'054	—	0'090	—	0'042
Total average .. .	49'093	48'957	1'566	1'545	1'513	1'474	1'458	1'438
Difference .. .	—	0'136	—	0'021	—	0'039	—	0'020

F. S. SHIVER, South Carolina.—Determinations on line (a) were made by a modification of the Lindo-Gladding method as follows:—"After PtCl_4 has been added the solutions are evaporated to dryness on the water-bath, both of which are heated not quite to boiling. A little water is now added, about 1 c.c. in case of superphosphates, and about 2 c.c. in case of muriates, sulphates, and kainits. Five volumes of 95 per cent alcohol for each one of water are now introduced; the whole thoroughly mixed and allowed to stand one hour. Filtration and washing with 80 per cent alcohol and the NH_4Cl solution follow in the usual way." Results on line (b) were obtained by strictly following the official method.

THOS. L. BLALOCK, North Carolina.—Results on line (a) and (b) were obtained by evaporating until crystallisation took place on cooling. Those on line (c) were evaporated to dryness and moistened with water.

W. S. SWEETSER, Pennsylvania.—I find that when NaCl is used more washing is required in order to get uniform results.

H. B. McDONALD, Maryland.—The use of NaCl is certainly unnecessary.

ELWYN WALLER, New York.—Some of the results may differ from others on the same sample because of differences in percentage of moisture in the sample at different times, but the conclusion I should make is that without NaCl there was a tendency to irregularity, and, on the whole, lower results. The directions for the Lindo-Gladding method in the Bulletin do not seem to give the idea as to the amount of ammonium oxalate required. It says, "a little." I find that 10 grms. needed over 50 c.c. of (1 to 24) solution for complete separation of CaO . I analysed potassium by the same methods (theoretically = 9.90 per cent); result with NaCl = 9.816; result without NaCl = 9.836, which seems to be essentially the same.

H. J. WHEELER, Kingston, R. I.—I am very glad you are to take up the point in question, for past results indicate the possible benefits from such a course.

W. J. WILLIAMS, Wilmington, Del.—I may state that on several occasions I have tested this question and have found that if the potash after treatment with half-strength sulphuric acid is thoroughly ignited to whiteness, so that no free sulphuric acid is left, the addition of NaCl makes no more difference in results than will be found in ordinary analytical differences. I believe it is unnecessary.

The mass of evidence here presented furnishes strong and convincing proof that the use of NaCl is unnecessary in potash determinations.

Dr. Gladding in 1885 presented his results to his association upon chemically pure sulphate of potash. Three determinations without NaCl gave him 100.95, 102.81, and 101.45 per cents respectively of sulphate of potash. Three determinations of the same salt made with the addition of NaCl gave 100.01, 100.16, and 99.95 of sulphate potash, obviating the inaccuracy he supposed to exist from the presence of free sulphuric acid when the NaCl was not used.

Two hundred and nine results obtained by twenty-two chemists show no advantage in the use of NaCl . Instead of obtaining something which was not potash and hence higher figures without NaCl , the general tendency has been to lower results when NaCl was omitted. This difference was quite small, but is present in a large majority of the determinations, and is naturally to be expected, if the NaCl is not needed, on account of the difficulty of washing out the sodium salt. About two-thirds of the analysts who took part in the work obtained slightly higher figures with NaCl than without it, the reverse of Dr. Gladding's experiences. In about three-fourths of the determinations the differences between with and without NaCl , by the same chemist, were less than one-tenth of one per cent, and in about half of the results the differences were less than one-twentieth of one per cent.

Recommendations.

The following recommendations are made:—

(1) In superphosphates, page 187, second line, in place

of the words "a little oxalate of ammonia" insert "a sufficient quantity of oxalate of ammonia to throw down all lime present."

On lines numbers nine and ten strike out the words "5 c.c. of a solution of pure NaCl (containing 20 grms. NaCl to the litre), or its equivalent of dry salt."

On line number eleven change the word "are" to the word "is."

(3) Sulphate of potash, kainit, &c., page 187, second and third lines, in place of the words "a little oxalate of ammonia," insert "a sufficient quantity of oxalate of ammonia to throw down all lime present."

On page 188, second line from top, strike out the words "add 0.25 grm. of NaCl ," and insert the word "add" between "and" and "15 c.c."

On page 188, fifth line from top, strike out the words "0.25 grms. NaCl and."

Page 188, fifth line. Put the word "all" in place of the word "these," and in the sixth and seventh lines, after the words "to remove all the double chloride of platinum and sodium," add the words "if present."

It is also recommended that the reporter on potash for the coming year put himself in communication with the Association of Experiment Stations in Germany, and any other accessible official chemists in other countries, and secure, as far as possible, their co-operation in our comparative work of the coming year.

Bearing on this subject the following quotations are translated from a letter of the German Kali syndicate of July 29th, 1892:—

"As yet, the Association of Experiment Stations of the German Empire has not accepted any definite methods for potash determination. Not many stations use the Stassfurt methods. A variety of methods are in use according to the preference given by different chemists. We have made a request of the Association of Agricultural Experiment Stations of the German Empire to take steps for securing uniformity in this question. Privy Councillor Maerker, who is President of the Committee on Fertilisers, has already declared that he will make a motion at the next convention in September to test the Stassfurt methods and eventually to recommend their introduction."

Further on will be found the methods of potash determination used at the Anhalt mines at Stassfurt, Germany, as communicated by their chief chemist, Dr. Zimmerman, with his criticisms of other methods. His work, while most excellent with the Stassfurt method, shows want of experience with the Lindo-Gladding method, as in these analyses the difference between the highest and lowest is over one per cent, a difference for which the method is certainly not to blame, when so many American official chemists are constantly working it with results equally as close as he obtains with the Stassfurt method.

We wish accurate methods and quick ones, and are always ready to grasp anything good. The Stassfurt method is submitted to the Association with the suggestion that it be taken up and studied through our next reporter on potash. If it is equally as good as the Lindo-Gladding, and much quicker, as claimed, it will be very valuable.

The London CHEMICAL NEWS (vol. lxx., pp. 22, 32) contains an interesting article by Drs. Gooch and Hart upon the spectroscopic detection and estimation of potassium.

There is a point in the determination of potash which is not given the proper weight and attention by manufacturers, and it is that of mixing. Unmanipulated potash salts give analytical chemists far less trouble, as a rule, than mixed fertilisers.

To mix fifty pounds of rough muriate of potash with a ton of fertiliser, as is sometimes done, and secure a perfect mixture, is almost impossible. Weights and measures are handled roughly and quickly, and some manufacturers appear to believe that badly mixed goods,

after standing and becoming disintegrated by the sulphuric acid, actually become well mixed. If a solution is made up from a fertiliser, and several determinations made from that same solution, they tally beautifully; but make separate weighings from your supposed well-mixed sample, and results never check so well. Manufacturers think a "wet mix" ought to be perfect, but as all the ingredients are weighed independently for each ton, and in the South negroes usually do this work, and bricks, in some establishments, are used as weights, it is easy to see how each ton must vary, and the only wonder is that the goods run as uniformly as they do. To illustrate this, fourteen analyses are here given of goods made by the same formula and claimed to be identical, which were drawn out of separate batches from a large and well-equipped factory. These samples show imperfect mixing, whether from too rough weighings or bad manipulation it is difficult to decide, with only small samples drawn by other parties. Attention is also called to the varying amounts of moisture, insoluble phosphoric acid, and ammonia. Moisture varies 8.30 per cent, insoluble phosphoric acid 4.13 per cent, ammonia 0.77 per cent, and potash 0.95 per cent.

Moisture.	Insol. P_2O_5 .	Avail. P_2O_5 .	Ammonia.	Potash.
14.95	2.33	9.95	2.37	2.16
15.00	2.24	10.30	2.29	2.19
13.50	4.22	9.34	2.26	2.03
16.85	1.60	10.17	2.33	2.24
16.55	2.49	9.41	2.29	2.12
16.60	2.43	9.21	2.25	2.20
16.55	2.62	9.41	2.12	1.70
16.25	2.36	9.79	2.00	1.80
17.75	1.00	10.90	1.93	1.60
18.85	0.41	9.82	2.33	2.33
19.45	0.26	10.11	2.53	2.30
21.80	0.09	9.76	2.44	2.55
19.05	0.90	9.46	2.50	2.35
18.10	0.64	10.11	2.70	2.45

(To be continued).

NEW METHODS FOR QUANTITATIVE ANALYSIS.*

By A. BAUMANN.
(Concluded from p. 237).

THE separation of sulphur has an injurious effect, in as far as it occludes starch iodide, and thus produces an excessive consumption of solution of thiosulphate.

In presence of merely very small quantities of sulphides, the expulsion of hydrogen sulphide may be omitted without injury. The sulphur which is separated on the decomposition of the polysulphides does not interfere on account of its finely pulverulent form.

Whilst the determination of the mineral acids succeeds without difficulty, the separation of the iodine by the organic acids is only effected by degrees. The transformation in solutions of tartaric and oxalic acid is not complete until twenty-four hours have elapsed. For acetic acid a still longer time is required. The determination of organic acids by the iodometric method appears, therefore, injudicious, but Gröger regards it as probable that the method may be applicable if the organic acids are caused to act upon the iodine salts with the aid of heat.

Baumann utilises the reaction which ensues between free acid and a mixture of potassium iodate and iodide for the determination of free mineral acids in the gas-volumetric way, proceeding as follows:—

He puts into the larger space of the development vessel of the azotometer a knife-point full (from 1 to 2 grms.) of

very finely powdered potassium iodate, dissolves it in a little water, adds about 10 grms. potassium iodide, and then runs in an accurately measured quantity of the acid, which must be greatly diluted. Iodine is separated and remains dissolved in the excess of potassium iodide. The liquid is diluted to about 40 c.c. if its volume is smaller. The attached glass cylinder is charged with hydrogen peroxide and potassa lye in the manner previously described, the stopper is closed, and after the temperature has become equalised the iodine is determined gas-volumetrically. The number of the c.c. of gas found is multiplied with the number in the author's hydrogen table, and thus the weight of the hydrogen of the acid is obtained.

In order to find the weight of the acid the product is multiplied by the equivalent concerned.

No very strong acids can be directly determined by the gas-volumetric method, but only acids of about the strength of those which are titrated with decinormal alkali.

Of acids at 3 to 6 per cent we take 2 c.c. for analysis if the measuring tube of the azotometer holds only 50 c.c. A double quantity may be used if a burette holding 100 c.c. is available. Stronger acids are made up with water to a given volume, and an aliquot part is used for determination. A larger quantity of weaker acids may be used, e.g., 30 to 60 c.c. of decinormal acid.

According to Baumann, the determination of the organic acids may be effected if certain conditions are observed. Tartaric, oxalic, and acetic acids liberate an equivalent quantity of iodine if they are heated to 70° for thirty minutes with the mixture of potassium iodide and iodate.

NOTES ON SOME ANCIENT DYES.*

By EDWARD SCHUNCK, Ph.D. F.R.S.

THE fragments of ancient dyed fabrics which I have examined I owe to the kindness of Mr. R. D. Darbishire. They are specimens from a lot found by Mr. Flinders Petrie, in a tomb at Garob, Lower Egypt, supposed to date from 400—500 A.D. They were used apparently for filling the mummy cases where required, not strictly speaking as grave clothes. My object in examining them was to ascertain, if possible, what were the materials employed in producing the various colours seen on them. The fabrics examined consisted almost entirely of wool. Here and there in the warp of some of the specimens were threads, conspicuous for difference in colour, consisting of linen. The following colours could be distinguished:—Blue, yellow, green, red, maroon, purple or claret, black. I will take them in the order named.

Blue.—The colour of the fabric was a dull medium blue. On treatment with hot caustic lye a great part of the wool dissolved. The residue, which was dark blue, having been filtered off, washed, and dried, was treated with boiling aniline, to which it communicated a bright blue colour. The blue solution having been filtered boiling, deposited on cooling a quantity of blue crystalline scales, which, after being filtered off, washed with alcohol, and dried, were found to consist of indigo-blue. On being heated in a tube they gave a sublimate of regular crystals, blue by transmitted, copper coloured by reflected, light; they dissolved in concentrated sulphuric, giving a blue solution, and the solution in aniline showed the absorption-spectrum of indigo-blue. It is evident, therefore, that indigo in some form or other was the material used in dyeing this colour.

Yellow.—The colour of the patches dyed yellow was so evidently faded, and showed so little intensity, as to make it very uncertain whether analysis would lead to any precise result; the examination was therefore omitted.

Green.—Of the material dyed this colour, I had but a

* *Zeit. für Angew. Chemie und Zeit. für Analytische Chemie.*

* From *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, vol. V. Series 4.

small quantity, but it was sufficient to allow of some conclusion regarding the means whereby the colour was produced. On being treated for some days with dilute hydrochloric acid it imparted to the latter a deep yellow colour. The portion left by the acid, after being washed and dried, yielded indigo-blue on treatment with boiling aniline. It is probable, therefore, that the colour was produced by first dyeing the fabric with indigo, then treating with some mordant, such as alum, and, lastly, dyeing with some yellow colouring matter, most likely of vegetable origin. With the small quantity of material at my disposal, I found it impossible to ascertain the nature of the yellow colouring matter employed.

Red.—This was the most pronounced, and at the same time the most interesting, of the colours examined. The colour of the fabric was a full deep red. It might be called a Turkey red: the dye, in fact, proved on examination to be a kind of Turkey red as having the characteristic properties of that dye.

On being burnt, the fabric left a considerable quantity of ash, consisting of calcium sulphate, alumina, aluminium phosphate, ferric oxide, and silica. A large portion of this ash no doubt represents the mordant employed in producing the colour. On treatment with hot dilute hydrochloric acid the fabric lost its red colour and became yellow. After removal of the acid by washing with water, and pressing between blotting paper, treatment with boiling alcohol deprived the wool of the greater part of the yellow colour, a faint tinge only being left. The deep yellow alcoholic liquid obtained left on evaporation a reddish-brown amorphous residue. This, on being treated with a boiling solution of alum, dissolved in part, yielding a pink fluorescent liquid, which had exactly the same colour, and showed precisely the same absorption bands as a solution of purpurin from madder in alum liquor. On adding hydrochloric acid to the pink solution and heating, the colouring-matter was precipitated in orange-coloured flocks, the liquid becoming almost colourless. The flocks after being filtered off and washed with water dissolved easily in boiling alcohol, yielding a yellow solution, which, on spontaneous evaporation, left a quantity of dark yellow needles arranged in rosettes. These needles dissolved in caustic alkali, giving a cherry-red solution, which showed the absorption bands of purpurin. The solution, on exposure to air and light, became colourless.

Some of the precipitated colouring-matter, on being employed in the usual way for dyeing a bit of calico to which various mordants had been applied, yielded colours exactly like those obtained with purpurin from madder, *i.e.*, the alumina mordant gave a bright red, the iron mordant dull purple to black tints. The matter left undissolved, after repeated treatment with boiling alum liquor, was still highly coloured. It dissolved easily in alcohol, the solution leaving on evaporation a brown amorphous residue, which remained soft even after long standing. This residue consisted for the most part of fatty matter, but it also contained some colouring-matter insoluble in alum liquor. That this colouring-matter was alizarin seemed probable, since the colour which the mixture imparted to alkaline lye resembled that of an alkaline solution of impure alizarin.

These experiments lead to the conclusion that the red colour of the fabric was produced by dyeing with some kind of madder, either wild or cultivated, the fabric having been previously treated with a mixed aluminous and ferric mordant, and then probably oiled,—that it was, in fact, really a kind of Turkey red.

Maroon.—The dull chestnut colour of this fabric presented a striking contrast to the bright red of the preceding. Its constitution was, however, similar. Having treated it in the same way as the other, I found that the colouring-matter must have been derived from madder; fatty matter was also present, but the mordant contained a larger proportion of ferric oxide,—a fact which sufficiently explains the brown tint of the dyed fabric.

Purple.—The fabric in which this colour was seen was made up of a pale yellow warp, and a weft of a dull purple or claret colour. The latter colour was found to be due to an intimate mixture of red and blue, for the threads, on examination under the microscope, were seen to consist partly of red, partly of blue fibres, the former predominating. The two sets of fibres had, of course, been mixed before spinning. The blue fibres were certainly died with indigo, the red probably with madder.

Black.—The colour of the black fabric, like that of the green, was a compound of two colours, one overlying the other. Under the microscope the individual threads appeared grey. On treatment with a mixture of alcohol and hydrochloric acid they changed colour, a yellow liquid being obtained, while the fabric itself now appeared blue, and after washing and drying yielded indigo by appropriate treatment. The yellow alcoholic liquid was found to contain purpurin. The colour may be supposed to have been produced in the following manner:—The woollen fabric having first been dyed blue was mordanted, to use a modern phrase, and then dyed with madder, the two colours together producing the effect of black.

THE ELECTROLYSIS OF METALLIC FORMATES.*

By HILL SLOANE WARWICK.

THE facility with which many metallic formates could be reduced to the metallic state by heat, or in the case of silver and mercury, even by the action of light, having led to the hope that they might be employed with particular advantage in electrolysis, the following series of experiments were made upon solutions of copper, zinc, and cadmium formates, in order to ascertain the effect of dilution, temperature, and pole separation, as well as the conditions necessary in order to effect their quantitative estimation and separation. The current was generated by a battery of ten cells, of the "crowfoot" type, each cell being 3·1 d.m. in height, by 1·9 d.m. in diameter, and having a capacity of two litres; the dimensions of the zincs were 1·5 c.m. by 1·5 c.m., and of the radiating copper plates constituting the positive pole 1·5 c.m. by 1·5 c.m. By means of this battery a comparatively uniform current of 2·8 c.c. electrolytic gas per minute was generated after the cells had been in use for some time.

The strength of the current was measured by means of an ordinary voltmeter, and was ascertained before and after the completion of the experiment. For the deposition of small quantities of metal, thick platinum foil electrodes were used, 3·8 c.m. wide, and immersed to the depth of 3·8 c.m. in the solution. For quantities above 0·05 grm. they were unsatisfactory, the metal showing a great tendency to separate in a spongy condition at the edge. In the earlier determinations a platinum dish was used, weighing about 67 grms., and having a capacity of 150 c.c.; in the later ones a dish weighing 117 grms., and with a capacity of 275 c.c., was employed. The results obtained with the larger dish were necessarily somewhat less exact than with the one of smaller size. The positive pole consisted of a thick platinum wire, the lower portion of which was wound into a horizontal spiral. In some of the separations it was found expedient to substitute for the spiral a small platinum crucible 2·5 c.m. in height and 2·8 c.m. in diameter, closed by a cork, through which passed a copper wire in contact with the bottom of the crucible. In order to regulate the distance between the poles, a filter stand was used, having inserted on its movable arm an ordinary binding screw, to which the positive pole was attached.

The following formates were prepared:—

* Read before the American Philosophical Society, November 6, 1891. From the *Proceedings of the American Philosophical Society*, xxix., No. 136.

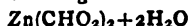
Copper Formate.

This salt was made by precipitating cupric oxide from a hot solution of copper sulphate, by means of caustic potash; the precipitate was washed by decantation until free from traces of potash; it was then dissolved in formic acid having the sp. gr. 1.015, obtained in the usual way from oxalic acid and glycerin, through which a current of steam was allowed to pass in order to prevent too great a rise of temperature, with the consequent production of decomposition products; the salt was allowed to crystallise out by spontaneous evaporation in a current of warm air, and re-crystallised. An abundant crop of large blue monoclinic crystals was obtained, having the composition $\text{Cu}(\text{CHO}_2)_2 \cdot 4\text{H}_2\text{O}$, effervescing in dry air, soluble in eight parts of water, and changed by boiling to the sparingly soluble basic salt $\text{Cu}(\text{CHO}_2)_2 \cdot 2\text{Cu}(\text{HO})_2$.

Zinc Formate.

A solution of ordinary crystallised zinc sulphate was treated with an excess of sodium carbonate, heated almost to boiling, freed by decantation from soluble impurity, and dissolved in hot formic acid. The solution was evaporated down and allowed to stand, after filtering off a slight precipitate that formed on boiling, and which gave the iron reaction with potassium sulphocyanate.

Monoclinic prisms having the formula—



separated out, isomorphous with the cadmium salt, permanent in the air, and soluble in twenty-four parts of water at ordinary temperature.

Cadmium Formate.

This salt was prepared by dissolving cadmium obtained by distillation *in vacuo*, in nitric acid, neutralising with a hot solution of potassium carbonate, washing by decantation until free from soluble carbonate, and dissolving in formic acid. Large monoclinic crystals separated out, having the composition $\text{Cd}(\text{CHO}_2)_2 \cdot 2\text{H}_2\text{O}$, permanent in the air, readily soluble in water.

(NOTE.—The formulæ of copper and cadmium formates are given as follows:— $\text{Cu}(\text{CHO}_2)_2$ and $\text{Cd}(\text{CHO}_2)_2$ in the last edition of Watts' "Dictionary of Chemistry," differing from all other authorities. Experiments made to settle the question resulted in the formulæ assigned, which is in accordance with the ones usually given).

Lead Formate.

Solutions of lead acetate and sodium formate were mixed and allowed to stand. Large white anhydrous rhombic crystals gradually separated out in radiating needles, sparingly soluble in cold water, more readily in hot, but with partial decomposition into free acid, and a basic salt of variable composition.

Cobaltous Formate.

A hot solution of cobaltous sulphate was neutralised with caustic soda solution, washed by decantation until free from all but traces of the precipitant, dissolved in formic acid, filtered, and allowed to evaporate in a current of warm air. The salt separated in crusts, consisting of indistinct crystals having the composition—



dissolving with difficulty to a reddish coloured solution.

Manganous Formate.

This salt was prepared from manganous carbonate precipitated from a hot solution of manganous sulphate, by means of sodium carbonate added to alkaline reaction and decanted as rapidly as possible until free from all except very slight traces of soluble salts. It was then dissolved in formic acid and allowed to crystallise very slowly. The crystals thus obtained were allowed to re-crystallise. The crystals are small pale reddish monoclinic prisms, soluble in fifteen parts of water, and contain two molecules of water of crystallisation.

Nickel Formate.

A solution of nickel chloride was treated with a slight excess of sodic hydrate, washed several times by decantation with hot water, dissolved in acid, and evaporated down. A greenish crust formed, made up of very small bright green needles— $\text{Ni}(\text{CHO}_2)_2 \cdot 2\text{H}_2\text{O}$.

Ferric Formate.

Ferric chloride was treated with excess of a solution of ammonia, washed with hot water, and allowed to digest in formic acid at a temperature which was not allowed to exceed 70°, until the hydrate of iron had completely dissolved, which required several hours. The deep red solution was allowed to crystallise by spontaneous evaporation. Yellowish red needles crystallising in radiating tufts separated out, which formed a light loose coherent powder. When dried at a moderate temperature, it was readily soluble in cold water with an acid reaction. Aqueous solutions on warming became turbid from the partial decomposition of the salt into ferric hydrate and free acid. A similar decomposition takes place in solutions at ordinary temperatures after standing for some time. (The foregoing salt was made in preference to ferrous formate on account of its greater solubility).

Mercuric Formate.

Mercuric oxide was dissolved in formic acid, but on warming the solution slightly it decomposed into the very sparingly soluble white mercurous formate, carbon dioxide, and formic acid, according to the following equation:—



and—



The precipitate was grey in colour from the presence of free mercury. The tendency to decompose is such that in solution at ordinary temperatures these changes take place readily in the light and, with more slowness, even in the dark. The "ous" salt comes out in minute shining crystals, very insoluble in water, and on continuous warming becomes entirely converted into free mercury. The formates of silver, bismuth, and tin are not prepared, as they were not considered available for various reasons.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, November 7, 1892.

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE following were elected Members of the Royal Institution:—Miss Emily Drummond, J. J. Duveen, Esq., Edward Johnson, Esq., George Blundell Longstaff, M.D., F.R.C.P., Robert Dobie Wilson, Esq.

The Special Thanks of the Members were returned to Mr. Thomas G. Hodgkins, of Brambletye Farm, Setauket, Long Island, New York, for his most valuable gift of \$100,000 (£20,523 6s. 11d.).

The Special Thanks of the Members were returned to the Goldsmith's Company for their generous grant of £1000 "for the continuation and development of the valuable original research which the Society is engaged in carrying on; and especially for the prosecution of investigations on the properties of matter at temperatures approaching that of the zero of absolute temperature."

The Special Thanks of the Members were returned for the following Donation: Mr. F. D. Mocatta, £50, for carrying on Investigations on Liquid Oxygen.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

NOTICES OF BOOKS.

Theine versus Tannin; or, China Tea versus Indian and Ceylon Tea. By STUART CRANSTON (Glasgow). London: W. B. Whittingham and Co.

THE title of this remarkable pamphlet might lead any cursory reader to suppose that Indian and Ceylon tea contained no theine! Yet the author admits (p. 6) that Indian tea contains *more* theine than that from China. According to the analyses quoted, the Chinese teas are also much poorer in tannin; but this is not an original difference: it depends merely on the process of manufacture. The pamphlet before us admits that the excess of tannin might be eliminated with advantage. There are also some other difference not here emphasized. Chinese tea is worked up by hand, whilst the Indian leaf is scarcely touched except by machinery. Now, anyone who knows the hands of John Chinaman would greatly prefer any articles which he had *not* touched.

The use of tea along with albumenoid foods—as in the so-called “tea-dinner”—is a great mistake. Whatsoever truth there is in Mr. Cranston's pamphlet might, we submit, have been put in a more patriotic manner.

CORRESPONDENCE.

NEW SILVER ORE.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS, vol. lxxv., p. 42, is a “Note on the Recent Discovery of a New Silver Ore,” by Mr. H. N. Warren, in which he asserts that the well-known argentiferous kaolin of Broken Hill, N.S. Wales, was first noticed this year by some travelling mineralogists. As a matter of fact, large quantities of specially rich kaolin were first noticed in April, 1885, by Mr. W. Jamieson, one of the original developers of the Broken Hill on the south half of Block 12. Fifty tons were sent to Melbourne while the B. H. Proprietary Company was being floated in July, 1885, and yielded 750 ounces of silver to the ton.

Shortly after its discovery the ore was known to contain chloride, bromide, and iodide of silver.—I am, &c.,

W. PERCY WILKINSON,
Assistant to the Government Analyst.

Melbourne, Victoria, October 4, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 18, October 31, 1892.

Observations on M. Berthelot's Communication presented at the Last Session of the Academy of Sciences.—M. Schloesing.

Reply to the Foregoing Paper by M. Berthelot.—A controversy on priority in the announcement of the condensation of nitrogen upon soils by the agency of microphytes.

The Dissociation of Barium Peroxide.—H. Le Chatelier.—The dissociation of barium peroxide is a phenomenon less simple than it is supposed. It requires

the intervention of watery vapour and the action of presence of a melted mixture of barium hydroxide and barium peroxide. Hence the conditions of the tension of dissociation are not rigidly fixed.

A Limited Reaction.—Albert Colson.—In studying the action of sulphuretted hydrogen upon metallic salts dissolved in benzene free from water, the decomposition is not complete, and it gives rise to a peculiar state of equilibrium. A very small quantity of water alters the results and ensures total decomposition.

The Fixation of Free Nitrogen by Plants.—Th. Schloesing and Em. Laurent.—In the conditions of the author's experiment, oats, colza, and potatoes did not fix free nitrogen in a measurable quantity.

Purification of Sewage by Ferric Sulphate.—A. and P. Buisine.—The authors conclude that it is possible to treat large volumes of sewage continuously by means of ferric sulphate, and to obtain valuable products from the mud.

Ptomaines Extracted from Urine in Erysipelas and Puerperal Fever.—Dr. A. B. Griffiths.—The former ptomaine is a white substance forming orthorhombic lamellæ, soluble in water, with a slightly alkaline reaction. Its formula is $C_{11}H_{13}NO_3$. The ptomaine found in puerperal fever has the same properties, but its composition is $C_{23}H_{19}NO_2$. Both these ptomaines are intensely poisonous.

Hermerythrin: A Respiratory Pigment found in the Blood of Certain Worms.—Dr. A. B. Griffiths.—There are in the blood of invertebrate animals at least four respiratory pigments containing iron in their molecule.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., Nos. 15 and 16.

On Acetone-Resorcine.—H. Causse.—The compound of acetone and resorcine is in small prismatic crystals, anhydrous, and fusible at 212° to 213° . It is insoluble in water, benzene, chloroform, and dry ether, but soluble in alkaline hydrates and carbonates. Its composition, dried at 30° , is $C_{15}H_{16}O_4$. The reaction is general. Besides resorcine, pyrogallol and pyrocatechine combine very readily with acetone, but hydroquinone forms no combination.

Light Oils obtained in the Distillation of Bog-Head.—A. Brochet.—Among the numerous ethylenic carbides which may be formed during pyrogenation, those of the linear chain exist almost alone. There are only small quantities of isobutylene and traces of trimethylene. Hexylene is the highest term of the series which is formed in this medium. Then follows benzene, toluene, dipropentilene, and finally coal-tars, which on distillation give products of an offensive odour.

Preparation of Zinc, Manganese, and Cadmium Sulphites.—G. Denigès.—The composition of these salts is: zinc sulphite, $(SO_3Zn)_2 + 5H_2O$; manganese, $SO_3Mn + 2H_2O$; and cadmium, $(SO_3Cd)_2 + 3H_2O$.

On Quinine Iodomethylates.—E. Grimaux.—This memoir does not admit of useful abstraction.

Syntheses in the Ethylenic Hydrocarbides under the Influence of Zinc Chloride.—Jean Kondakoff.—This extensive memoir also is not adapted for abstraction.

In Reference to a Note by M. Hantzsch on Carb-acylacetie Ether.—P. Genviesse.—A controversial note.

Facts to Contribute to the History of Gum Arabic.—A. Béchamp.—The author, in common with Dubrunfaut, holds that the molecule of gum consists of dextrorotatory and levorotatory members. If this hypothesis is admitted, the explanation of the fact that the

nitro-gums are dextrorotatory follows from the theory of M. Guye. In these compounds the nitric acid is connected by substitution with the dextrorotatory term or terms, and determines the dextrorotation of the molecule which was originally levorotatory.

Researches on Nickel and Cobalt.—M. Lachaud and Ch. Lepierre.—In a former communication they described the action of ammonium bisulphate ammonium on the salts of iron (*Comptes Rendus*, April 11th, 1892). They now describe the substances obtained with nickel and cobalt.

Action of Ammonium Sulphate upon Glass.—M. Lachaud and Ch. Lepierre.—The action of ammonium sulphate seems to be specific, and this action is the more curious as it disaggregates the glass at a relatively low temperature.

Condensation of Chlorobenzile with Phenol and with Mono- and Dimethylaniline.—M. St. Kempinski.—The substance obtained is insoluble in water, in acids, and in ligroine, but very soluble in water, alcohol, benzene, &c., and in caustic alkalis. It is a red powder, which does not appear to possess tinctorial properties.

Action of Phosphorus upon Copper.—M. Granger.—The compound obtained by the author corresponds to the formula Cu_3P_2 . If ignited in an inert gas they lose phosphorus and leave as a residue Abel's phosphide, Cu_3P .

Mercury Phosphide.—M. Granger.—The compound obtained is Hg_3P_4 .

Change of Sign of the Rotatory Power.—J. A. Le Bel.—This paper does not admit of useful abstraction.

Tri- and Tetra-sulphonic Indigotine Acids.—P. Juillard.—All the author's analyses establish the presence of tri- and tetra-sulphonic indigotine acids in the state of mixture. The colouring matter obtained is doubtless identical with Bailley's purple-blue.

Direct Transformation of Aniline into Nitrobenzene.—M. Prudhomme.—The group NH_2 of aniline is directly converted into NO_2 . This transformation is very interesting since we know only one procedure for passing from aniline to nitrobenzene, that of Sandmeyer.

Certain Ethers of Gallic Ether and of Dibromogallic Acid.—Alex. Bietrix.—An account of ethyl dibromogallate and methylgallate.

Gummy Matters and the Peptic Matters. A New Organised Ferment of Cherry Gum.—F. Garros.—If cherry gum is left with water in a flask very full and stoppered with wadding in one and a half months the cherry gum is entirely dissolved, and there is a deposit at the bottom of the flask consisting of members smaller than those of beer-yeast. It is this ferment which has effected the solution of the cherry gum.

MISCELLANEOUS.

The Late Professor Stas.—According to the *Chem. Zeitung*, the Belgium Academy of Sciences unanimously petitioned the Government to purchase the valuable apparatus and chemicals of the departed *savant* as of high historical scientific value, and deposit them in a public museum so as to obviate the danger of their being dispersed. The Academy petitioned also for the necessary funds for a new edition of all the memoirs of Stas which are no longer to be procured in the book-trade. After a long delay the Academy received a complete refusal. It was alleged that "the schools were sufficiently supplied with apparatus and preparations." This reply gives a decisive measure of the level which Belgian statesmen have reached as regards Science. We thus see that the English Government does not stand isolated in being unfavourable to Science and her followers.

Society of Arts.—The following courses of Cantor Lectures will be delivered during the coming session of the Society of Arts:—"Prof. Vivian Lewes, 'The Generation of Light from Coal-Gas, and its Measurement,'" on Nov. 21, 28, Dec. 5, 12; Dr. J. A. Fleming, 'The Practical Measurement of Alternating Electric Currents,' on Jan. 30, Feb. 6, 13, 20; Prof. W. Chandler Roberts-Austen, C.B., F.R.S., 'Alloys,' March 6, 13, 20; Mr. Lewis Foreman Day, 'Some Masters of Ornament,' April 10, 17, 24, May 1; Mr. C. Harrison Townsend, F.R.I.B.A., 'The History and Practice of Mosaics,' May 8, 15.

MEETINGS FOR THE WEEK.

MONDAY, 21st.—Society of Arts, 8. "The Generation of Light from Coal-gas," by Prof. Vivian B. Lewes.
Medical, 8.30.
TUESDAY, 22nd.—Royal Medical and Chirurgical, 8.30.
Institute of Civil Engineers, 8.
Photographic, 8.
WEDNESDAY, 23rd.—Society of Arts, 8. "Cremation as an Incentive to Crime," by F. Seymour Haden, F.R.C.S.
Geological, 8.
THURSDAY, 24th.—Royal, 4.30.
Institute of Electrical Engineers, 8.
FRIDAY, 25th.—Physical, 8. "Experiments in Electrical Magnetic Fields, Constant and Varying," by E. C. Rimington and E. Wythe Smith.

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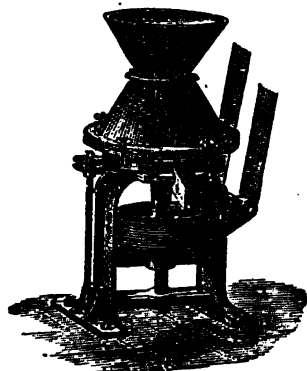
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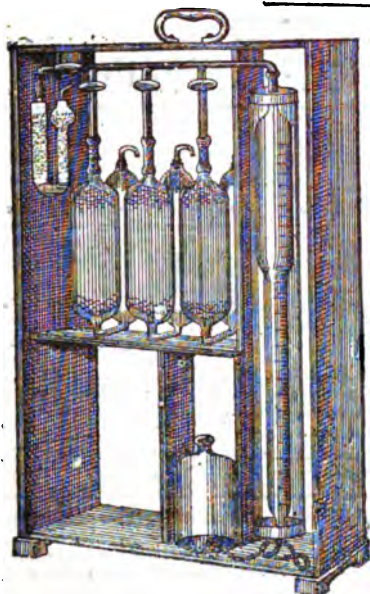
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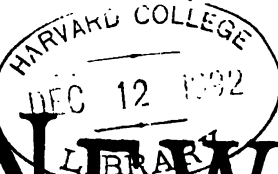
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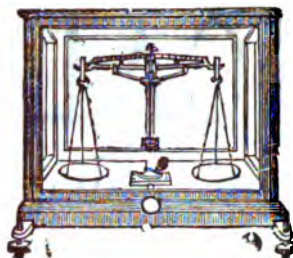
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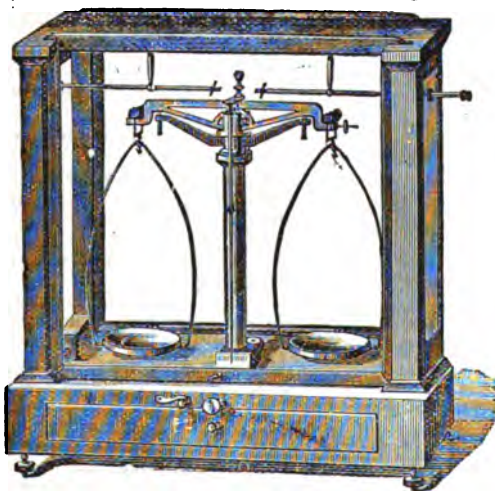


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VOL. LXVI., No. 1722.

THE VOLUMETRIC DETERMINATION OF THE ALKALOIDS.

By ALFRED H. ALLEN.

THE paper of M. Barthe, reproduced from *Comptes Rendus*, which appears in the *CHEMICAL NEWS* (vol. lxi., p. 223) ought not to be absorbed into chemical literature without a protest. M. Barthe believes that his observations are novel, but such of them as are accurate have been established previously by several observers, and are now well known to chemists interested in the alkaloids.

The actual facts respecting the behaviour of the alkaloids with phenolphthalein are stated in the following passage from a paper read by me before the Chemists' Assistants' Association in January, 1891, and printed in the *Pharmaceutical Journal* ([3], xlii., 772) a few weeks later:—

"It is interesting to observe that phenolphthalein and Poirrier's blue, CLB, which may be used as indicators for very feeble acids, are absolutely indifferent to the majority of the alkaloids and organic bases. Even aniline and pyridine, which have such strongly marked basic characters, are perfectly neutral to phenolphthalein. The same is true of strychnine, quinine, aconitine, and, with the limitation already mentioned, morphine. Hence the salts of these bases, such as hydrochloride of aniline, sulphate of quinine, and nitrate of aconitine,* can be titrated with caustic alkali and phenolphthalein, just as if the respective acids were in an uncombined state. According to E. Léger, cicutine and codeine are exceptions to the general rule of indifference of the alkaloids to phenolphthalein; and, according to P. C. Plugge, nicotine and conine also exhibit an alkaline reaction. A curious exception to the general behaviour of alkaloids is also presented by atropine and its isomers (as also hematropine), which in the free state strongly redden phenolphthalein. This property, however, does not exist in alcoholic solution—a fact which marks a curious distinction between these alkaloids and the mineral alkalies, the alcoholic solutions of which react perfectly with phenolphthalein."

I do not claim any originality for the above statements, which simply express the results of various observers supplemented by my own experience; but the following applications of this principle are novel. In the analysis of a mixture of cinchona alkaloids, the cinchonidine is usually precipitated from a neutral solution by potassium-sodium tartrate, and the precipitate washed with cold water (thereby causing an uncertain loss), dried, and weighed. If, instead, the precipitate be washed once with a saturated solution of the precipitant (which has very little solvent action), and the filter containing the precipitate of cinchonidine tartrate and the adherent Rochelle salt be immersed in boiling water, the alkaloid can be determined in a few minutes by adding a drop of phenolphthalein solution and titrating with N/20 caustic alkali. As Rochelle salt is perfectly neutral to phenolphthalein, and as alkaloidal tartrates act just like an equivalent amount of free tartaric acid, the weight of alkaloid can be readily calculated from the measure of standard alkali used. An exactly similar method is applicable to the treatment of the precipitate of quinidine hydriodide.

In sharp contrast to the indifference of nearly all the alkaloids to phenolphthalein is their behaviour with methyl-

orange. To this indicator most of the alkaloidal salts are rigidly neutral, and hence all the alkaloids and organic bases of which the behaviour has hitherto been examined—except urea, caffeine, theobromine, and (perhaps) aniline—may be titrated with methyl-orange and a standard mineral acid, and with much greater facility than when litmus is used.

In titrating an alkaloid with methyl-orange it is rarely convenient to employ an aqueous solution of the base. A solution in proof spirit can be used, but the indicator is much less sensitive under such conditions. I have found it preferable, especially when the alkaloid is much coloured, as is frequently the case in assaying bases directly extracted from their sources, to dissolve the alkali in a little ether, chloroform, amyl alcohol, or other suitable immiscible solvent. The solution is placed in a small stoppered cylinder, together with a few c.m. of water coloured with a drop of methyl-orange solution. On then gradually dropping in the standard acid and agitating thoroughly after each addition, it is easy to observe the end of the reaction, as the interfering colouring-matter remains in the immiscible layer and presents a marked contrast to the red colour of the aqueous liquid. By using ether as a solvent, and titrating with N/50 hydrochloric acid, I have obtained very satisfactory determinations of aconitine and its allies, even when working on as little as 0.030 grm.

A similar plan can be adopted for the titration of the morphine crystals obtained in the assay of opium, amyl alcohol being used as the solvent; or the alkaloid can be simply dissolved in excess of standard acid, and the solution titrated back with alkali, using methyl-orange as the indicator of neutrality.

Sheffield, November 14, 1892.

NOTE ON THE ESTIMATION OF OLEIN.

By L. DE KOWINGH, F.G.S.

THE *Analyst* (vol. xvii., p. 118) contains an article on the determination of olein by Mr. O. Hehner, and the author comes to the conclusion that the process founded upon the relative solubilities of the fatty lead salts in ether is utterly untrustworthy. This opinion will perhaps cause works chemists to distrust a process which I am not in the least inclined to give up; a process which I still consider to be, under certain conditions, one of the most elegant and accurate methods to be met with in organic commercial analysis.

It is far from my intention to criticise Mr. Hehner's iodine figures, as these are no doubt very accurate in their way; but my object in writing these lines is to point out how to apply the process when great accuracy is required. Nobody must expect to get a reliable result when the oleic acid is largely exceeded by the fixed fatty acids; in fact, it is not unlikely that in such a case the operator will find none at all. But the remedy is a simple one. A proper equilibrium must be restored, and this is best done by dissolving the fatty acids in boiling alcohol and searching for the oleic acid in the mother-liquor from which the bulk of the solid acids has crystallised out.

Analysts familiar with the process must have noticed that the clear ethereal solution of the lead oleate sometimes gets turbid and deposits a more or less abundant flocculent precipitate. This precipitate is, I have good reason to believe, a basic lead oleate, as the normal lead salt seems to behave in a slight degree like normal bismuth nitrate. If now the analyst notices that such has taken place, or if the extraction has not gone quite so readily as usual, the best way is to decompose the residual lead soap by means of hydrochloric acid, to re-crystallise the liberated acids from alcohol, and to once more apply the process to the mother-liquor. In fact, the well known principle of re-dissolving and re-precipitating should be applied.

* Ordinary nitrate of aconitine is not a neutral salt; it contains $B_2(HNO_3)_2$.

As regards the lead salts of palmitic and stearic acid, they are absolutely insoluble, as may be easily proved by adding ammonium sulphide to their supposed ethereal solution. Of course, I am not prepared to say what a few months' extraction in the Soxhlet may do, as I believe that even barium sulphate might disappear at last, but under normal conditions the ether process will be found a very suitable one for those fats which are mainly composed of stearin, palmitin, and olein.

In conclusion, I should like to ask Mr. Hehner to ascertain for himself the iodine absorptions of the oleic acids from tallow, lard, and also once more for cotton-seed oil, for which I have found the figures 90, 93, and 135 when using the process described in *The Analyst*, vol. xiv., 64-65.

ON CHROMIUM CAST STEEL.

By SERGIUS KERN, M.E., St. Petersburg.

At the last meeting of the Iron and Steel Institute (October, 1892), Mr. R. A. Hadfield contributed a highly valuable paper on "Alloys of Iron and Chromium." We were especially interested with the handsome results obtained by Mr. Hadfield in the manufacture of chromium steel projectiles, as we took a prominent part in the manufacture of the same in Russia, at the Poutiloff Iron and Steel Works, St. Petersburg. We worked by the process adapted by the French works of J. Holtzer, Unieux, Loire.

Great care must be taken in casting ingots for projectiles; rising ingots are rejected. Such metal contains only small amounts of silicon and manganese. Good sound metal contains on the average 0.18 per cent of silicon and 0.20 per cent of manganese. The sum of phosphorus and sulphur is not to exceed 0.03 per cent (sulphur better not more than 0.015 per cent). Chromium steel has a pasty appearance, but if prepared in a Siemens gas crucible furnace, has enough heat in itself to remain fluid in the crucible for ten to fifteen minutes, after the withdrawal of the latter from the furnace.

Care must be taken in handling the ingots just only cast. Throwing them on wet ground, or placing them where the wind, rain, or snow can cool them, should be avoided, as cracks in the ingots may result. The best method is to bury the cast ingots in ashes. For the forging of ingots between stamps the metal should be heated not higher than 1000° C.; the same temperature is to be observed during the annealing of the forged projectiles before they are sent to the turning and boring lathes.

In 1890 we commenced the manufacture of 12-inch projectiles for the navy. The specimens from the annealed ingots gave the following results:—

Diameter of specimen, 16 m.m.
Length of specimen, 100 m.m.

Specimen. Nos.	Elastic limit. (In kilogrms. per square m.m.)	Breaking strain. (In kilogrms. per square m.m.)	Elongation. Per cent.
1.	49.5	93.1	7.2
2.	54.1	95.4	8.1
3.	41.5	88.1	7.3
4.	40.3	85.6	8.0
5.	45.3	95.5	6.5

From one of the reception lots, viz., 100 12-inch projectiles, three were selected by the Government inspectors and gave the following results.

Only two shells were fired at the polygon of Ochta, near St. Petersburg. The 16-inch compound armour plate was manufactured at the Kolpino Works by the Cammell method; the gun was made at the Obouhoff Steel Works. Both works belong to the Government, and are situated some few miles off St. Petersburg.

The two shells penetrated the plate and were found on the other side of the plate at a distance of—

First projectile 7000 feet.
Second projectile 5250 feet.

They showed no cracks, and altered only very slightly in their dimensions.

We used ferrochrome coming from Boucau (France), containing only 0.08 per cent of phosphorus and 0.03 per cent of sulphur. It is a very pure alloy. The Russian ferrochrome prepared by the Demidoff Works cannot be used in the manufacture of projectiles. It contains a rather poor quantity of chromium and too much of phosphorus, as shown by our analyses made on different samples:—

Sample No.	Chromium.	Phosphorus.
1.	35.30 per cent.	0.411 per cent.
2.	38.81 "	0.409 "
3.	40.45 "	0.421 "
4.	40.50 "	0.558 "

On the other hand, the Boucau samples are very rich in chromium, containing not less than 49 per cent up to 60 per cent of the metal.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1892.

By WILLIAM CROOKES, F.R.S.,

and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolitan Water Act, 1871.

London, November 8th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from October 1st to October 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Throughout the month of October the water supply to the Metropolis continued to be of excellent quality, and was found not to differ appreciably in character from that of the preceding month, or materially from the supply of the past six months inclusive, taken as a whole. Of the entire rainfall of the month, amounting at Oxford to a little over 3 inches, fully 2½ inches fell during the last five days of the month, with the result of bringing the river into flood, but not affecting the character of the then supply. The entire series of the 182 samples examined were found to be well-filtered, clear, and bright; and their degree of colour-tint to be low for the season of the year.

The following Table of the results furnished by the Thames-derived supply, taken for illustration, shows the smallness of the extent of the monthly variation at present noticeable in the amounts of organic matter present in the water,—the excess of organic carbon in the Octo-

ber supply above the mean for the six months' supply, or 0.01 part in 100,000 parts of the water, being quite infinitesimal.

Thames supply.	Ratio of brown to blue tint.	Oxygen required for oxidation.	Organic carbon per 100,000.	Organic carbon per 100,000.
	Means.	Means.	Means.	Maxima.
Past 6 months	10.4 : 20	0.039	0.117	0.155
September ..	15.5 : 20	0.042	0.118	0.145
October ..	15.0 : 20	0.047	0.127	0.155

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

SEPARATION OF MALIC ACID FROM SUCCINIC, CITRIC, AND TARTARIC ACIDS.

By C. MICKO.

THE process depends on the behaviour of the acids with baryta water.

Free succinic, citric, or tartaric acid is not completely precipitated by baryta water either in cold or heat. But the precipitation succeeds under especial circumstances if the acids are present in the form of neutral or acid potassium salts.

In concentrated solutions of acid or neutral potassium succinate an excess of baryta water effects an incomplete precipitation in the cold. On boiling, or on prolonged heating, to a temperature near the boiling-point, succinic acid is completely eliminated, save in very trifling traces. After standing at rest for half an hour the precipitate takes a granular crystalline texture, but if allowed to stand for a week perceptible quantities pass again into solution.

The solutions of potassium citrate, acid or neutral, behave with baryta water in a similar manner. The precipitate, which appears in the cold, if slowly heated to gentle ebullition, is suddenly converted into a voluminous paste, which is a characteristic of citric acid.

Potassium tartrate, neutral or acid, behaves differently. A complete precipitation is not produced by an excess of baryta water either in heat or cold. After standing for twenty-four hours at the ordinary temperature, a large part of the tartaric acid is precipitated. If we then pass into the filtrate a slow current of carbonic acid until the reaction is neutral or faintly alkaline, and then add anew an excess of baryta water, after standing for twenty-four hours at the ordinary temperature a complete precipitation of the tartaric acid ensues. The experiment succeeds at a gentle warmth, but not in heat.

In mixtures of potassium succinate, citrate, and tartrate no complete precipitation of the acids is obtained. Even after introducing carbonic acid into the filtrate and a renewed addition of baryta water, traces of all the three acids could still be detected after standing for twenty-four hours. It seems as if the liberated potassa prevents complete precipitation. The attempt was consequently made to neutralise the potassa by an addition of barium acetate, and in this manner a complete precipitation of the several acids was effected.

A mixture of the acids, however, did not give a complete precipitation, even in presence of potassium acetate, if the carbonic acid was introduced in the cold. But it was found advantageous under such conditions to introduce carbonic acid in heat until the liquid became neutral or very faintly alkaline. But as no complete precipitation of the acids was effected even in this manner, the main quantity of the baryta was thrown down in heat by the introduction of an excess of carbonic acid, and the filtrate was evaporated down to a small residue. If this residual liquid was again treated in the manner above described, the filtrate obtained was free from tartaric, citric, and succinic acid.

In solutions of potassium malate, baryta water produces a faint turbidity only after prolonged boiling, and no precipitate occurs in presence of alkaline acetates.

On the basis of these experiments the author proposes the following method for separating malic acid from the succinic, citric, and tartaric acid:—

The solution which contains the acids as potassium salts, and which should have a faint acid reaction, is evaporated down in a flask until it amounts only to 10 to 15 c.c., mixed with 0.5 grm. barium acetate and an excess of baryta water, and gradually heated to ebullition. This is kept up for two minutes, with frequent agitation, and, after cooling, the flask is closed and allowed to stand for from twelve to twenty-four hours. The bulky precipitate is then filtered off and washed with baryta water. The washing must not be continued too long, as otherwise the precipitate begins to re-dissolve.

The filtrate is then heated to incipient ebullition, the heating is interrupted, and carbonic acid is then introduced until the reaction is neutral or slightly alkaline. An excess of baryta water is added, the mixture is again allowed to stand for twelve or twenty-four hours, and the precipitate is filtered off and washed with baryta water.

The filtrate is heated and treated with a current of carbonic acid to precipitate the excess of baryta, and the precipitate is filtered off and washed with hot water. The filtrate is then, after the addition of two to three drops of acetic acid (to prevent separation of baryta during concentration), evaporated down to 10 or 15 c.c., and again heated to remove the last traces of succinic, citric, and tartaric acids. Carbonic acid is passed into the warm liquid without filtration until the reaction is neutral or faintly alkaline, and after adding baryta water until the reaction is distinctly alkaline it is again allowed to stand from twelve to twenty-four hours. It is then filtered, and the precipitate is washed with baryta water as above. The filtrate thus obtained contains all the malic acid, and is free from the three other acids.

The baryta is precipitated in heat with carbonic acid, the barium carbonate is washed with hot water, the filtrate is concentrated to a small volume (after the addition of two to three drops of acetic acid), and the remaining baryta is precipitated with a slight excess of potassium carbonate. The filtrate acidulated with acetic acid is evaporated down to a small residue, another drop of acetic acid is added, and, as soon as it is cold, 5 c.c. of a solution of lead acetate (1 : 5), previously acidulated with acetic acid, and 120 c.c. of alcohol at 80 per cent are poured in, stirring continually.

The precipitation is effected in a flask, which is stoppered and allowed to stand for forty-eight hours. The large excess of alcohol is necessary, and much potassium acetate is present in proportion to the potassium malate, and the former salt prevents complete precipitation if the addition of alcohol is insufficient.

The precipitate is filtered off and washed with alcohol at 80 per cent, at first cold and then hot. The filtrate, which is often turbid, is heated in a flask with a reflux cooler until the solution is clear. The flask is then stoppered and set aside for forty-eight hours. The small quantities of lead bi-malate separated out are washed with cold alcohol. The dried precipitates are united, dissolved in hot alcohol, and the lead is separated with sulphuric acid. The weight of malic acid is calculated from the lead sulphate obtained.

The results are very satisfactory. Though the values are too low (about 96.3 per cent in place of 100), precipitation is preferable to the calcium chloride method, since the latter is not available in presence of potassium acetate.

The author has tried direct precipitation with lead acetate in pure solutions of potassium malate. The results are rather too high (about 102 per cent), as small quantities of lead acetate are carried down.

If lead malate is precipitated in heat with alcohol we certainly obtain a fine granular precipitate, but the results

are much too high, since the precipitate partially melts and the inclosed lead acetate cannot be removed by washing.—*Zeitschrift für Analytische Chemie*.

ATTEMPT AT A GENERAL METHOD OF ORGANIC SYNTHESIS.

By RAOUL PICTET.

THE object of this research is to define in a precise manner a general method for obtaining synthetically any natural substance whatever. The way to be adopted to fix the programme of the successive necessary reactions follows from a primary hypothesis, which will serve as a postulate in these researches. In this preliminary paper space does not permit us to expound anything more than this hypothesis,—the foundation of all our study on chemical synthesis. We shall then give a series of experimental verifications of the fundamental hypothesis. Lastly, we shall describe the first applications of this theory to divers chemical syntheses of the aromatic series.

Fundamental Hypothesis.

We admit that all physical and chemical phenomena result from the conflict of two attractions: the attraction of *matter for matter* and the attraction of *matter for ether*. According to the distance of the atoms among themselves, the attraction of matter for matter receives the names of *gravitation*, *cohesion*, *affinity*. We do not know the value of the Newtonian function applied to *cohesion* or to *affinity*. We admit that the atoms are immersed in the ether but remain impenetrable to this fluid. In virtue of this fact they are subject to the laws of the principle of Archimedes, as they always displace their own volume of ether.

The attraction of matter for ether follows a special law different from the Newtonian law, extending to all distances. Our fundamental hypothesis may be thus expressed:—On reducing every chemical phenomenon to the action of two masses of matter falling upon each other along the right line passing through their centres of gravity, we admit that the two functions of the distances representing the two attractions enable us in every case, and without exception, to find three positions of equilibrium upon this right line—that is to say, three positions where the resultant of the two attractions is null. Further, the equilibrium is stable in the two extreme positions and instable in the mean position.

[The remainder of this memoir cannot be reproduced without constant reference to the diagram given in the original].—*Comptes Rendus*, cxv., p. 708.

THE DETERMINATION OF PHOSPHORIC ACID IN BASIC SLAGS.

By DR. ADOLF F. JOLLES.

THE views on the solvent in the determination of phosphoric acid in basic slags differ widely from each other. We may particularise two directions, one of which recommends the samples to be opened up with concentrated sulphuric acid and the other with hydrochloric acid.

At a meeting of Austrian managers and officials of agricultural experimental stations, held at Vienna on August 30, 1890, Dr. von Lorenz recommended the use of Maercker's process exactly as it had been proposed at Bonn Congress of the Experimental Stations in 1889. I have had repeated opportunity to analyse basic slags both by the molybdenum method and by Maercker's process, and I always obtained differences in the percentage of phosphoric acid which were proportional to the percentage of lime. These differences are to be referred to the well-

known fact that the gypsum liberated on opening up the slags with concentrated sulphuric acid incloses particles of calcium phosphate which are thus withdrawn from the solution. I have found similar losses of phosphoric acid when using hydrochloric acid.

Last year H. and E. Albert, of Biebrich, on the basis of numerous experiments, have recommended the following method for determining total phosphoric acid in basic slags, and have introduced it into the laboratory of their works:—

Five grms. of the finely-ground slag are moistened with a little water in a flask of the capacity of 500 c.c. and boiled upon the sand-bath with 40 c.c. of hydrochloric acid at 16°–20° Bé. The mixture is boiled until there remain only a few c.c. of a thick paste of silicic jelly, allowed to cool, and a little water is added. It is then shaken until the thick clots of silicic acid are very finely divided, made up to 500 c.c. with water, and filtered. 50 c.c. of the filtrate are mixed with 15 c.c. of Joulie's solution (*i.e.*, 400 grms. citric acid made up to 1 litre with ammonia of specific gravity 0.9), and then precipitated in the ordinary manner with magnesia mixture, ignited, and weighed. There is no danger of obtaining silica in the magnesia precipitate, since many experiments have proved that the condensation of the hydrochloric solution to a thick jelly is sufficient to render the silica insoluble. If a standard solution of uranium is at hand we dissolve (if the presence of silica is suspected) the moist precipitate on the filter in a little nitric acid, and titrate in the usual manner.

I have had this process and, as a check, the molybdenum method carried out in numerous analyses of basic slags in my laboratory, with the result that the Albert method, both gravimetrically and volumetrically, yielded far too high results in comparison with the molybdenum method. The cause of these discrepancies can only be sought for in the imperfect elimination of the silica.

I cannot in my analyses confirm the above quoted statement of H. and E. Albert, since I have always been able to recognise the presence of silica in the precipitates of magnesia. I have, then, dissolved the magnesia precipitate in hydrochloric acid, evaporated it to dryness, heated the residue to 120° in the air-bath, re-dissolved in hydrochloric acid, and weighed the silica.

The differences varied according to the time of boiling, and I obtained results agreeing with those of the molybdenum method only on boiling the basic slag meal in hydrochloric acid, evaporating completely to dryness, and heating in the air-bath to 120°. This method may thus be modified by evaporating the silica to perfect dryness, retaining the further course of the analysis.

As for the volumetric determination, I have dissolved the moist precipitate of ammonium magnesium phosphate in a little nitric acid, neutralised it with ammonia, dissolved it in acetic acid, and titrated with solution of uranium. The results obtained have, by accident, coincided with the gravimetric results according to Albert, so that I at first believed that no silica was present in the precipitate of ammonium magnesium. In fact, however, I found in every precipitate ponderable quantities of silica; therefore, according to the check titration with uranium solution I should have obtained less phosphoric acid than by weighing, which was not the case. There occur here also sources of error which act in opposite directions and which may even mutually compensate each other.

The most important defect of this method lies in the untrustworthiness of the indicator. I have frequently observed that the brown colour does not appear at once, but not until the lapse of some minutes.

I believe that in the analysis of manures the motion accepted at the Congress of Chemists at Hanover in 1889 ought to be kept in mind, according to which "the volumetric determination of phosphoric acid is regarded as no longer adequate to the demands of the age and is declared untrustworthy."

For the volumetric determination of phosphoric acid in basic slag, I venture to propose the following modification of the method of H. and E. Albert:—

Five grms. of fine slag-meal is moistened with a little water in a capsule boiled with 40 c.c. of hydrochloric acid at about 20° Bé, and evaporated to perfect dryness. The residue is heated to 120° in the air-bath, moistened with hydrochloric acid when cold, taken up in water, and filtered. The filtrate is made up to 500 c.c., 50 c.c. of which are mixed with citrate solution, and the phosphoric acid is precipitated in the ordinary manner with magnesia mixture, when the precipitate is dried, ignited, and weighed.

With this procedure I have obtained results which agreed fairly with those of the molybdenum method. In cases where the analyst wishes to check himself or other chemists, and in disputed cases, the molybdenum method is exclusively admissible.—*Zeit. fur Anal. Chemie.*

REPORT ON POTASH.*

By Dr. GEORGE F. PAYNE, Atlanta, Ga.,
State Chemist of Georgia
(Concluded from p. 254).

A DESCRIPTION AND CRITIQUE OF VARIOUS METHODS OF POTASH ANALYSIS.

Methods of Potash Analysis as used in the Mines of Anhalt.

(1) DETERMINATION of potash alone in carnallite, kainit, and sylvinit: 100 gr. of the well mixed sample are put into a graduated flask, holding 1000 c.c., and dissolved by boiling with 500–600 c.c. water, acidulated with 10 c.c. hydrochloric acid. The purpose of adding hydrochloric acid is to bring polyhalite in solution, that might be present in the salts, and which is difficult to dissolve in pure water. After dissolving and cooling, the flask is filled up to the mark. The solution after thorough mixing is filtered through a dry filter. 100 c.c. of the filtrate, corresponding to 10 gr. substance, are put into a 500 c.c. flask by means of a pipette. After the addition of 200–300 c.c. water, the solution is heated to boiling and the sulphuric acid accurately precipitated with normal chloride of barium solution, containing 104 gr. of the dry salt in one litre. The volume of the precipitate is calculated from the amount of barium solution used, and from the specific gravity of the barium sulphate. After cooling, the flask is filled up with water so much above its mark as equals the volume of the calculated barium precipitate, and, after thorough mixing, the solution is filtered again through a dry filter. 50 c.c. of this filtrate, corresponding to 1 gr. substance, are evaporated upon the water-bath with a sufficient amount of platinum chloride. The residue of potassium-platinum chloride is washed with 90 per cent alcohol, dried at 120°, and weighed.

(2) If it is desired to determine separately the quantity of potash present in the form of sulphate, and in the form of chloride, as for example in kainit, and in sulphate of potash, or, if it is to be determined whether potassium sulphate is in combination with a proportionate amount of magnesium chloride, as in kainit, or in combination with magnesium sulphate alone, as in schoenit, it becomes necessary to determine besides potash the percentage of chlorine, sulphuric acid, lime, magnesia, the total alkalies, water, and the residue insoluble in water. For this purpose, 100 gr. of the sample are dissolved, the solution is filtered, the filter washed, and the filtrate made up to one litre; a part of the liquid is taken for the determination of sulphuric acid, by precipitating with barium chloride, and another part for the determination of lime and magnesia. For the determination of the alkali chlorides, 100 c.c. of the solution, corresponding to

10 gr. substance, are acidulated with hydrochloric acid, and after heating to boiling, the sulphuric acid is completely precipitated with barium chloride, with the precaution of using not more of the barium solution than is necessary for the complete precipitation. 50 c.c. of the filtered solution, corresponding to 1 gr. substance, are evaporated to dryness in order to drive off the hydrochloric acid. Chloride of magnesium is decomposed by igniting with oxalic acid, or with oxide of mercury. After ignition, the residue is moistened with a little carbonate of ammonia for the purpose of rendering the calcium oxide that may have been formed into calcium carbonate.

The alkali chlorides, which are now entirely free from lime and magnesia, are weighed, and potassium chloride is determined by means of platinum chloride. The amount of chloride of sodium results by deducting chloride of potassium from the mixed chlorides. For the water determination, 5 gr. of the sample are ignited, and the loss of weight is determined. The ignited mass is dissolved in water, and for the purpose of determining the quantity of chloride of magnesium that may have been decomposed by the ignition, the percentage of chloride is determined by titration. The difference in the contents of chlorine before and after ignition is subtracted from the loss in weight, after allowance has been made for the absorption of oxygen and for the loss of hydrogen: the balance is water. The results obtained are calculated in the following manner:—From the total amount of the sulphuric acid found, that portion is deducted which is combined with calcium as calcium sulphate, the balance of the sulphuric acid is divided into two equal parts, for the purpose of calculating the contents of potassium sulphate and magnesium sulphate, according to the molecular proportion in which these salts are present in kainit and in schoenit. If there is an excess of potash left uncombined with sulphuric acid, then it is in the form of chloride of potash, likewise the amount of magnesia, uncombined with sulphuric acid, is to be reckoned as chloride of magnesia. The result of this calculation will tell how much potash is in the form of kainit (K_2SO_4 , $MgSO_4$, $MgCl_2$ with $6H_2O$), and how much of it is in the form of schoenit (K_2SO_4 , $MgSO_4$ with $6H_2O$) and in the form of chloride of potash. The sodium is reckoned as chloride of sodium.

(3) In calculating the contents of potash, of chloride of potash, and of sulphate of potash, from the weighed potassium-platinum chloride, the factors 0.1928, 0.3056, and 0.3566 are used, assuming that the atomic weight of platinum is 197.18.

(4) The two methods which have been described under Nos. 1 and 2, and which are in common use in the Stassfurt potash industry, i.e., the so-called precipitation method and the oxalic acid method, give almost identical results. The first method, however, deserves preference on account of greater simplicity in cases where potash alone is to be determined. Finkner's method likewise gives results which agree well with the results obtained by the customary methods. It consists in evaporating the salt solution with a sufficient quantity of platinum chloride, without previously removing the sulphuric acid, reducing the potassium-platinum chloride, and weighing the metallic platinum.

The following are the results of comparative analyses, executed by order of the manufacturers of muriate of potash. The sample investigated was taken from a quantity of 36,948 cwts. of carnallite; the following are the results:—

- | | |
|--------------------------------------|----------------|
| 1. After the precipitation method .. | 22.02 p.c. KCl |
| 2. After the oxalic acid method .. | 22.03 " " |
| 3. After Finkner's method .. | 22.01 " " |

In another sample from 75,582 cwts. carnallite the following results were obtained:—

- | | |
|--------------------------------------|-----------------|
| 1. After the precipitation method .. | 17.88 per cent. |
| 2. After the oxalic acid method .. | 17.88 " " |

* For the Association of Official Agricultural Chemists of the United States.

In a third sample from 97.435 cwts. of carnallite the contents of chloride of potassium were as follows:—

1. After the precipitation method .. 18.44 per cent
2. After the oxalic acid method .. 18.38 ..

Another method of potash determination which is used in many agricultural experiment stations, among them the Royal Station at Hohenheim in Wurtemberg, consists in precipitating the sulphuric acid and alkali earths with barium oxide and ammonium carbonate, and potash with platinum chloride. The results obtained with this method are, according to our experience, very inaccurate, and always too low. This is explained by the fact that it is impossible to precipitate sulphuric acid without at the same time precipitating some of the potash, unless it be in an acid solution.

A separation of the alkali earths, if potash alone is to be determined, is superfluous, for the reason that calcium and magnesium-platinum chloride are soluble in 90 per cent alcohol even with more facility than sodium-platinum chloride.

(7) There is a method in use and recommended by the Association of Official Agricultural Chemists of the United States of North America, termed the Lindo-Gladding method, for analysis of potash salts, and which has been reported to us by Dr. B. von Herff, of Washington. We subjected this method to a thorough test in our laboratory; the results obtained do not agree with those obtained by our customary methods, nor do they agree among themselves, if repeated analyses of the same sample are made. Moreover, this method is considerably more troublesome and subject to more errors than the precipitation method. An average sample of a large cargo contained:—

1. After the Stassfurt method.	1. After the Lindo-Gladding method.
1. 12.92 per cent K_2O .	1. 13.47 per cent K_2O .
2. 12.97 " "	2. 12.39 " "
3. 12.94 " "	3. 13.29 " "

Likewise the results of repeated analyses of a sample from a large quantity of sulphate of potash gave, according to the precipitation method, 52.7 per cent potash, while three determinations after the Lindo-Gladding method gave 53.40 per cent, 53.03 per cent, and 53.61 per cent. These figures presented will amply demonstrate the unreliability of this method.

THE QUANTITATIVE DETERMINATION OF RUBIDIUM BY THE SPECTROSCOPE.*

By F. A. GOOCH and J. I. PHINNEY.

In a recent paper issued from this laboratory (Gooch and Hart, *Amer. Jour. Science*, xliii., p. 448), the possibility of determining small amounts of potassium quantitatively by means of the flame spectrum was demonstrated. The work which we are about to describe was performed in the endeavour to see how far similar methods might be applicable to the quantitative determination of rubidium. It was shown in the former work that hollow coils of platinum wire may be adjusted to hold definite amounts of liquid, and that, by taking care to plunge the coil while hot into the liquid and to remove it from the liquid with its axis inclined obliquely to the surface, it is possible to take up constant amounts through a long series of experiments. It thus becomes possible to bring definite amounts of any soluble substance into a flame to be viewed spectroscopically. The potassium salt best adapted to spectroscopic use proved to be the chloride, and it was found to be advantageous to dry the coils over a hot radiator before introducing them into the flame. A large

Muencke burner gave the best sort of flame, an ordinary single prism spectroscope provided with an adjustable slit (the width of which we were able to fix by closing it upon wires of known diameter), and an observing telescope movable so that different portions of the spectrum might be shut out at will, served sufficiently well for the work. The coils were made of No. 28 platinum wire (0.32 m.m. in diameter), wound in about thirty turns to a spiral 1 c.m. long by 2 m.m. in diameter and twisted together at the ends to form a long handle. With the apparatus described it was found possible, under the most favourable conditions, to recognise the characteristic red line of the potassium spectrum when only 1-1000 m.grm. of potassium, in the form of the chloride, was brought to the flame. It appeared, furthermore, that a comparison of the brightness of two spectra produced in close succession could be made with all the accuracy to be anticipated in photometric measurements, and that therefore by gradual dilutions and successive testings a solution of potassium chloride of unknown strength could be brought to the point of containing as much potassium to the coil-full (and so, of course, to the c.c. or any other chosen volume) as a standard solution of known strength. By noting the final volume to which such an unknown solution was brought in the process of equalising its spectrum with that of the standard, its total contents in potassium was determined. In this manner the strength of solutions of pure potassium chloride proved determinable with accuracy, but when the effect of intermixing pure sodium chloride with the potassium salt was studied, it transpired that the brilliance of the potassium spectrum was markedly increased by the presence of the sodium in the flame, the maximum increase, which amounted to twenty per cent, appearing when the ratio of sodium chloride to potassium reached 100:1. It was found, however, that the practical difficulty of determining potassium in presence of sodium could be largely overcome by taking the precaution to bring the test solution and the standard to apparent equality as regards the potassium line, then to bring the solutions to an equality in respect to the sodium line by addition of sodium chloride to the standard, and finally to readjust the volumes of test and standard until the potassium lines were again equal. The accuracy of the determination of the potassium is, however, in spite of the precaution, somewhat affected by the presence of sodium,—the error, though, sometimes falling as low as 1-10 m.grm. in 10 m.grms., rising occasionally to 1 m.grm. in 15 m.grms. With the excellent gravimetric method which we possess for the determination of potassium recourse would, naturally, never be taken to the spectroscopic method except in cases where small absolute amounts are concerned, but in such cases the spectroscopic method may prove a convenience.

In the work upon potassium the observations of the red line were made in the ordinary laboratory in diffused light, but preliminary experimentation upon the rubidium spectrum immediately developed the fact that the blue lines are better to work by in the case of this element, and that a dark room becomes a necessity. For the experiments to be described pure rubidium chloride was prepared by many fractional precipitations by alcohol out of aqueous solutions, and in settling the question as to the coils which should be used, the choice fell upon the size holding 0.02 gm. of water and made of the No. 28 wire, the superior stiffness of these and consequent constancy in capacity giving them the advantage over smaller coils of finer wire, though the latter are capable of bringing out greater sensitiveness of the reaction. We found, for example, that under the most favourable conditions as to height of flame and width of slit, 0.0002 m.grm. of rubidium chloride produced the blue lines at the last limit of visibility, when the larger and heavier coil was in the flame; with a coil holding 0.006 gm. of water and made of very fine wire, the more immediate volatilisation of the chloride so increased the delicacy of the spectroscopic reaction that it was possible to see the lines from 0.00005

* From the *American Journal of Science*, vol. xlii., Nov., 1892.

m.grm. of the salt. These figures serve as an indication of the possible delicacy of this method of producing spectra, but it should be remembered that all eyes do not see the rubidium lines with equal ease.

In experimenting with rubidium sulphate in place of the chloride, the lighter coil appeared to lose its advantage in point of delicacy of the indication over the larger coil, possibly because the amount of metal introduced into the flame has less influence upon the rate of vapourisation of the less volatile sulphate, and the lines of the sulphate appeared equally distinct and of longer duration than those of the chloride; but, while we judged the sulphate to be rather preferable in qualitative work, our earlier preliminary quantitative experiments led us to abandon it for the purposes of our investigation on account of the great uniformity in the lines yielded by the chloride. We found it desirable in comparative tests of brightness to employ as the standard the lines given by amounts of the chloride not exceeding 0.0005 m.grm. to 0.0007 m.grm., to set the slit at a width of 0.2 m.m., and to bring the coils to the flame in sets of three—the first, usually a standard, serving to fix the position of the lines so that the comparative distinctness of the lines given by the other two might be the more readily determined. The tables below contain the record of an attempt to dilute a solution of the pure chloride to the strength of the standard solution under the guidance of comparative tests of the brilliance of the spectral lines yielded by the residue left upon the wires after the evaporation of the solutions taken up by coils of equivalent capacity. Dilutions were made in ordinary graduated cylinders of suitable capacity.

Experiment I.

Standard. Rubidium in a coil-full (1.50 c.m. ³).	Test (known to contain 10 m.grm. Rb.). Vol. in c.m. ³	Line of test compared with standard.
0.0005 m.grm.	200	Brighter.
" "	300	"
" "	350	"
" "	370	"
" "	390	"
" "	400	{ Brighter (faintly).
" "	400	"
" "	400	{ Doubtful. "
" "	410	{ Brighter (faintly).
" "	410	{ Weaker.
" "	420	{ Equally bright.
" "	420	{ Weaker.
" "	430	Invisible.

When the volume of the test solution reaches 400 c.m.³ the indications are, on the whole, that the solution is still stronger than an equal volume of the standard; and when the volume amounts to 420 c.m.³ it is safe to conclude from the indications that the test solution is the weaker. If the mean of the numbers representing these two volumes be taken as probably indicative of the volume at which the test and standard lines are at an equality, we have the estimated amount of rubidium in the test solution given by multiplying the volume in c.c. by the number of coil-fulls in 1 c.m.³, and the product by the amount of rubidium contained in a coil-full of the standard solution— $410 \times 50 \times 0.0005 = 10.25$ m.grm. The amount of rubidium actually taken in the test solution was 10 m.grm., and the error of the mean value assumed is 2.5 per cent +, between extremes corresponding to an error of 0 and 5 per cent +, respectively.

Experiment II.

Standard. Rubidium in a coil-full (1.50 c.m. ³).	Test (known to contain 10 m.grm. Rb.). Vol. in c.m. ³	Line of test compared with standard.
0.0005 m.grm.	340	Brighter.
" "	370	{ Equally bright.
" "	370	{ Brighter.
" "	390	{ Weaker.
" "	390	"

Found $\frac{370 + 390}{2} \times 50 \times 0.0005 = 9.5$ m.grm.
Taken 10.0 "
Error 0.5 " = .5 p.c.

Experiment III.

Standard. Rubidium in a coil-full (1.50 c.m. ³).	Test (known to contain 10 m.grm. Rb.). Vol. in c.m. ³	Line of test compared with standard.
0.0005 m.grm.	300	Brighter.
" "	360	Equally bright.
" "	380	Brighter.
" "	380	"
" "	390	"
" "	400	Weaker.
" "	410	"

Found $\frac{390 + 400}{2} \times 50 \times 0.0005 = 9.875$.

Taken 10.0
Error 0.125 = 1.25 p.c.

These results make it plain that when the comparison is made between solutions of pure rubidium chloride the spectroscopic method is capable of yielding fair approximations to truth. In the practical determination of rubidium, however, the question of the effect of the presence of sodium and potassium which naturally accompany it is of importance. Attention was therefore turned next to the consideration of this point, and the record of observations as to the influence of sodium upon the brightness of the rubidium spectrum is contained in the accompanying tabular statement.

Standard. Rubidium in a coil-full (1.50 c.m. ³) M.grm.	Test solution. Sodium in a coil-full, M.grm.	Comparison of lines of test by pairs.	Comparison of lines of test with standard.
0.00066	{ 0.00026 0.00260 0.00130 0.00260	{ Slightly brighter. Slightly fainter. Equally bright.	{ Brighter. Brighter.
"	{ 0.00260 0.00520	{ Equally bright.	{ Brighter.
"	{ 0.00260 0.00660	{ Brighter. Fainter.	{ Brighter.
"	{ 0.00260 0.00780	{ Brighter. Fainter.	{ Brighter.
"	{ 0.00260 0.01500	{ Brighter. Invisible on account of glare.	{ Invisible.

(To be continued).

THE
ELECTROLYSIS OF METALLIC FORMATES.*

By HILL SLOANE WARWICK.

(Continued from p. 256).

In order to ascertain the comparative accuracy of the results obtained by means of the ordinary gravimetric methods, as compared with those obtained by means of the current, a series of experiments was made with the

Copper (Determined as CuO).

Copper formate taken in grms.	Copper by theory in grms.	Copper in CuO formed.	Difference in percentage from theoretical. Per cent.
1. 0.8024	0.2252	0.2261	+0.39
2. 0.7924	0.2226	0.2232	+0.27
3. 0.7963	0.1984	0.1982	-0.10
4. 0.7963	0.1984	0.1979	-0.25

* Read before the American Philosophical Society, November 6, 1891. From the *Proceedings of the American Philosophical Society*, xxi., No. 136.

metals chosen for particular study. The gravimetric method adopted was the same for all three, namely, estimation as oxide conducted in the ordinary way.

The first two determinations were high, due perhaps to the efflorescence of the salt. All subsequent weighings were done in a covered watch-glass, and the results obtained corresponded closely with the theoretical.

In the following electrolytic depositions of copper, solutions of copper formate of known strength were used.

Copper (Determined Electrolytically).

	Copper present in solution.	Copper found.	Free formic acid.	C.C. H ₂ O.	Time in hours.	Difference in percentage from theoretical.
	Grms.	C.C.	C.C.			Per cent.
1.	0.1434	0.1438	10	125	46	+0.27
2.	0.1074	0.1075	15	125	16	+0.09
3.	0.0987	0.0988	5	125	17	+0.10
4.	0.0987	0.0987	10	125	16	0.00
5.	0.1074	0.1077	10	125	16	+0.27
6.	0.1057	0.1056	10	125	17	-0.09
7.	0.1057	0.1052	15	125	17	-0.47
8.	0.1101	0.1104	10	125	42	+0.27

In the above experiments a platinum dish was used at the negative pole, and the wire spiral as the anode. A current of 0.8 to 1.60 c.c. HO gas per minute was allowed to run over night. The poles were separated 2.5 c.m. Before cutting off the current the level of the liquid in the dish was raised by the addition of water, and the current allowed to act for an additional half hour. No further deposit of copper took place on the clean surface of the dish, indicating that the metal was completely precipitated. The current was then discontinued, the liquid quickly poured off, and the dish washed with hot water, being finally dried on a warm iron plate at a temperature not exceeding 100° C. The dish was then set aside for some time until it had acquired the temperature of the room and weighed. The solutions failed to give any indication, except the merest traces, of copper when tested with ferrocyanide of potassium. The time varied from sixteen to forty-six hours without materially affecting the result. No perceptible oxidation took place during drying, although the deposit was somewhat dark. It came out as a compact adherent coating, readily dissolving in nitric acid.

A comparison between the results obtained shows conclusively not only that the deposition of copper from its formate solution can be accomplished, but that it is fully as accurate as the ordinary gravimetric method.

Zinc (Determined as ZnO).

	Zinc formate taken in grms.	Zinc by theory in grms.	Zinc in zinc oxide found.	Difference in percentage from theoretical.
	grms.	grms.	found.	Per cent.
1.	0.5508	0.1875	0.1870	-0.26
2.	0.5508	0.1875	0.1876	+0.05
3.	0.5508	0.1875	0.1869	-0.31
4.	0.5508	0.1875	0.1872	-0.16

The four determinations made by the usual gravimetric method were estimated finally as zinc oxide, which, for purposes of comparison, have been converted into metal.

Zinc (Determined Electrolytically).

	Zinc present in grms.	Zinc found.	Free acid.	C.C. H ₂ O.	Time in hours.	Current in HO gas per minute.	Difference in percentage from theory.
	grms.	found.	C.C.				Per cent.
1.	0.0625	0.0614	none	100	16	1.8	—
2.	0.0625	—	10	100	16	1.8	—
3.	0.1250	—	15	100	16	2.0	—
4.	0.0818	0.0476	5	100	17	0.8	—
5.	0.0818	0.0816	15	100	17	1.7	-0.24
6.	0.0818	0.0819	15	100	16	1.7	+0.12
7.	0.0513	0.0513	25	100	16	1.7	—
8.	0.1026	0.1021	10	100	17	1.7	-0.48
9.	0.1026	0.1023	15	100	43	1.8	-0.29
10.	0.1006	0.1007	10	100	16	1.7	+0.09
11.	0.1006	0.1003	10	100	16	1.7	-0.29

The foregoing determinations of zinc formate were performed under a variety of conditions. 1, 2, 3, 4 were made with the dish as cathode and the wire spiral as the positive pole; the results, both with and without free acid, were unsatisfactory, the deposit being very spongy and failing to come out completely, as proved by testing the solution with potassium ferrocyanide. The dish was then made the anode, and the zinc was allowed to separate on the platinum crucible, which was made the negative pole. The amount of free acid varied from 10 to 25 c.c. The deposit was grey and adherent on the sides and bottom, but rather spongy at the periphery. Around the top of the crucible the metal was black in colour. The final determinations were accurate, but required the greatest care to avoid detaching loose particles of metal.

The deposit was not regular, the bottom of the crucible being more or less free from zinc on account of the accumulation of gas. The time of deposition averaged sixteen hours. Such currents as sufficed to separate copper were unsatisfactory, even when the electrodes were brought in close contact. In the determinations that were satisfactory, the current strength varied from 1.6 to 1.8 HO gas per minute, and the poles were close together.

Cadmium (Determined as CdO).

	Cadmium formate taken.	Cadmium by theory.	Cadmium in CdO found.	Difference in percentage from theory.
				Per cent.
1.	0.4224	0.1988	0.1983	-0.25
2.	0.4224	0.1988	0.1982	-0.30

Both results are somewhat too low, possibly owing to reduction of the oxide to metal and consequent loss by volatilisation.

Cadmium (Determined Electrolytically).

	Cadmium present in grms.	Cadmium found in grms.	Free acid.	C.C. H ₂ O.	Time in hours.	Difference in percentage from theoretical.
	grms.	found in grms.	C.C.			Per cent.
1.	0.0497	0.0498	15	100	16	+0.20
2.	0.0994	0.0996	10	100	18	+0.20
3.	0.0994	0.0991	10	100	16	-0.30
4.	0.1231	0.1228	10	100	44	-0.40
5.	0.1231	0.1229	10	100	17	-0.16
6.	0.0984	0.0984	10	100	16	—
7.	0.0984	0.0985	10	100	16	+0.10
8.	0.1004	0.1005	10	100	16	+0.09
9.	0.1004	0.1002	10	100	17	-0.19

The dish was used as the negative electrode, the spiral as the positive, except 1, in which the cadmium was deposited on the crucible, the dish serving as the anode. The distance between the poles was 2.5 c.m. The variations in the conditions of the experiments noted above caused no noticeable difference in the results. The deposit was not apparently oxidised by moderate warming. Current 1.25 to 1.5 c.c. HO gas per minute.

The solutions were tested for cadmium at the conclusion of each experiment, but none was found, proving that the metal was completely deposited. It formed a firm and adherent coating, white in colour, with a bright metallic lustre.

1. Influence of Dilution upon the Precipitation of Copper.

	Copper present in grms.	Copper found.	Free acid.	C.C. H ₂ O.	C.C. HO gas per minute.	Time in hours.
	grms.	found.	Drops.			
1.	0.0717	0.0199	3	100	1.75	1
2.	0.0358	0.0111	4	100	1.75	1
3.	0.0179	0.0057	4	100	1.75	1
4.	0.0089	0.0028	4	100	1.75	1
5.	0.0044	0.0014	4	100	1.75	1
6.	0.0022	0.0006	4	100	1.75	1
7.	0.0011	0.0002	4	100	1.75	1

The distance between the poles was 2.5 c.m. The area of the electrodes was (3.8 c.m. × 3.17 c.m.) × 2. The

deposition was performed in beakers having a capacity of 400 c.c., a height of 10 c.m., and 7.6 c.m. in diameter. The deposit was bright and adherent, and, although the amount of free acid present was very small, the metal was not spongy. The results obtained were in close accord with those assigned by theory, according to the law that the amount of metal deposited in a given time is proportional to the strength of solution.

II. The Influence of Temperature upon the Precipitation of Copper.

	Copper taken in grms.	Copper deposited.	Free acid.	C.c. H ₂ O.	Time in hours.	Temperature in degrees Cent.
1.	0.0211	0.0019	none	150	1	20°
2.	0.0211	0.0046	"	150	1	40°
3.	0.0211	0.0080	"	150	1	60°
4.	0.0211	0.0119	"	150	1	80°

The area of the electrodes was (3.5 c.m. × 3.8 c.m.) × 2. Distance between poles 2.8 c.m. The current gave 1.25 c.c. HO gas per minute. 1 was slightly spongy, and had a slight deposit of basic green salt at the top. 3 was somewhat dark and slightly spongy at the top, but adherent. The amount of metal deposited increased with rise of temperature as follows:—0.0027 grm. (20°—40°), 0.0034 grm. (40°—60°), 0.0039 grm. (60°—80°). The ratio of increase also rose with the temperature, being greatest between 60° and 80°. In the above series the determinations were made in neutral solutions; in the following, 15 c.c. of formic acid was added.

	Copper taken. Grms.	Copper deposited. Grms.	Free acid. C.c.	H ₂ O. C.c.	Time. Hours.	Temperature in degrees Cent.
1.	0.1057	0.0104	15	150	1	20°
2.	0.1057	0.0164	15	150	1	40°
3.	0.1057	0.0237	15	150	1	60°
4.	0.1057	0.0319	15	150	1	80°

The distance between the poles was 2.9 c.m., area of electrodes (3.5 c.m. × 3.8 c.m.) × 2, current strength 7.5 c.c. OH gas per minute. The ratio of increase was:—(20°—40°) 0.0060 grm., (40°—60°) 0.0073 grm., (60°—80°) 0.0082 grm. A comparison between the two series of results would indicate that the presence of dilute free acid in moderate quantity exercises no material influence on the amount of metal deposited, even at elevated temperatures.

III. The Influence of Pole Separation upon the Precipitation of Copper.

	Copper taken. Grms.	Copper deposited. Grms.	H ₂ O. C.c.	Time. Hours.	Distance between electrodes. C.m.
1.	0.1974	0.0133	700	1	1.58
2.	0.1974	0.0106	700	1	3.16
3.	0.1974	0.0093	700	1	4.75
4.	0.1974	0.0084	700	1	6.33
5.	0.1974	0.0078	700	1	7.91
6.	0.1974	0.0073	700	1	9.50
7.	0.1974	0.0064	700	1	12.66

The area of the electrodes was (3.8 c.m. × 3.48 c.m.) × 2, free acid pressure 10 c.c. 1 was slightly spongy. 7 was very close to the edge of the dish. The diminution was 1—2 0.0027 grm., 2—3 0.0013 grm., 3—4 0.0009 grm., 4—5 0.0006 grm., 5—6 0.0005 grm. The current gave 1.75 c.c. OH gas per minute.

The foregoing experiments were performed in a crystallising dish 15.2 c.m. by 7.6 c.m., with a capacity of 900 c.c. In the following series the determinations took place in a beaker 10 c.m. in height by 7.6 c.m. in diameter.

The current gave 1.75 c.c. oxyhydrogen gas per minute, area of electrodes (3.8 c.m. × 3.16 c.m.) × 2, free acid present 5 c.c. The diminution was:—1—2 0.0054 grm., 2—3 0.0040 grm., 3—4 0.0036 grm. In both series the rate of

	Copper taken. Grms.	Copper deposited. Grms.	H ₂ O. C.c.	Time. Hours.	Distance of electrodes. C.m.
1.	0.1434	0.0302	200	1	1.58
2.	0.1434	0.0248	200	1	3.16
3.	0.1434	0.0208	200	1	4.75
4.	0.1434	0.0172	200	1	6.33

diminution rapidly lessened as the distance between the electrodes increased.

Experiments made under conditions similar to the above, except that no free acid was present, were failures, the deposits being exceedingly spongy.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, November 11th, 1892.

MR. WALTER BAILY, M.A., Vice-President, in the Chair.

MR. PORTER was elected a member of the Society.

The Discussion on Mr. Williams's paper, "*The Dimensions of Physical Quantities*," was resumed by Dr. BURTON.

He remarked that the idea that so-called "specific quantities," such as specific gravity, are pure numbers, was an erroneous one, and liable to lead to difficulties. The specific gravity of a substance was of the nature of density, and was only a simple number on the convention that the density of water was taken as unity. If dimensions be given to specific quantities, their interpretation would, he thought, be easy when the rational dimensional formulæ were found.

Referring to prof. Fitzgerald's comments, he said that although the contention that all energy is ultimately kinetic could not be gainsaid, the distinction commonly drawn between kinetic and potential energy involved nothing contrary to this view and was useful and convenient in many cases. As to the dimensions of μ and k , he was inclined to favour Mr. Williams's views, for several considerations suggest that the two capacities of the medium are essentially different. Arguments to show that μ was probably absolutely constant in the ether, whilst k might be variable, were brought forward. Of the two systems of dimensions for μ and k suggested by Mr. Williams, that which made μ a density seemed preferable.

Prof. A. LODGE said he was greatly interested in propagating the idea that physical quantities are concrete, and therefore welcomed Mr. Williams's paper. He thought it desirable to keep some names for abstract numbers, and "specific gravity" should be one. If another name involving dimensions was required, "specific weight" or "weight per unit volume" might be used. Speaking of the dimensions of the various terms of an equation, he did not think it was usually recognised that in ordinary algebra or Cartesian geometry the principle of directed terms was rigidly adhered to; for, if directed at all, every term of such an equation was directed along the same line. In this respect ordinary algebra was more rigid than vector algebra. Even if circular functions were involved, as in polar co-ordinates, they had the effect of making the directions of the terms the same. Other instances of problems bringing out the same fact were mentioned.

MR. BOYS thought Mr. Madden had been arguing in a circle when he spoke of the astronomical unit of mass and deduced the dimensions of mass as L^3/T^2 from the equation $MLT^{-2} = M^2/L^2$, for it was quite impossible that this equation could be true unless γ (the gravitation constant) was introduced on the right-hand side. Mr.

Williams's method was quite the reverse; for he maintained that unless k and μ were introduced in the dimensions of electric and magnetic quantities, their dimensional formulæ could not indicate the true nature of those quantities, and hence were open to objection.

Mr. W. BAILY, whilst agreeing with Mr. Williams on most essential points, thought the total omission of L from dimensional formulæ made the expressions more complicated and less symmetrical. For example, such expressions as XY/Z , X^2 , and XYZ , which respectively represented undirected length, area, and volume, might with advantage be written L , L^2 , and L^3 respectively. The restriction of the dimensions of μ and k to those which give interpretable dimensional formulæ for electrical and magnetic quantities seemed scarcely justified. Both the systems proposed could not be right, and he thought it would be more in accordance with our present want of knowledge if a quantity, U , of unknown dimensions were introduced, such that μ or $k = U^2$ density, and k^{-1} or $\mu^{-1} = U^2$ rigidity. This would keep in view the fact that the absolute dimensions of quantities involving U were unknown. A list of the dimensions of the various quantities based on this arrangement was given.

Mr. SWINBURNE, referring to the conventional nature of many units, said great differences exist between the ideas held by different persons about such units. Starting with the convention that unlike quantities could be multiplied together, he might have 6 amperes flowing in an electric circuit under a pressure of 10 volts, and he might say he had 60 volt-amperes. The term "volt-ampere" could be regarded as indicating that the 60 was the numerical result of multiplying a number of volts by a number of amperes, or on the other hand it might be understood as a new unit, a *watt*, compounded of a volt and an ampere. Before Prof. Rücker's paper on "Suppressed Dimensions" was published, an electrician might have suggested measuring the length of a bench by sending an alternating current through it and determining its self induction, which he regarded as a length. Prof. Rücker, however, would say that this could not give the right result, for μ must be taken into account. He was inclined to think that dimensions were liable to mislead.

Referring to scientific writers as authorities, he said Maxwell had been careless in some cases, for he had sometimes given dimensional formulæ as zero, which really ought to have been $L^0M^0T^0$, or unity. In French text-books the errors had been corrected.

Mr. WILLIAMS, in reply to Mr. Madden's remarks about self induction being a length, pointed out that the subject might be looked at in two different ways, depending on whether one thinks of the *standard* of self-induction as the practical standard of measurement, or the *unit* of self-induction as a physical quantity. In the former case, the *standard* was a length, but in the latter the *unit* was a quantity of the same *species* as self-induction, the nature of which was, as yet, unknown. If its dynamical nature was known, then the absolute dimensions of all other magnetic and electric quantities would also be determined.

In answer to Prof. Fitzgerald's remarks, he said it was hardly likely that he should be unacquainted with the common view that kinetic and potential energies were ultimately quantities of the same kind, for it was a view with which he was quite familiar. The fact that they have the same dimensions was sufficient to show their identity, and the idea that all energy is ultimately kinetic was fundamental to his paper. This, however, did not imply that electrification and magnetisation are of necessity the same, and the suggestion that they may be the same was only one of several "probable suggestions," all of which were entitled to consideration. His chief reason for regarding Prof. Fitzgerald's suggestion as probably incorrect, was that it led to a system of dimensional formulæ incapable of rational mechanical interpretation, and containing fractional powers of the fundamental

units. Prof. Fitzgerald's system would make resistance an abstract number, and μ and k directed quantities, whereas the former was a concrete quantity, the two latter must be scalar in isotropic media. If he (Mr. Williams) had erred in treating electrification and magnetisation as different phenomena, he could only plead that he had done nothing more than follow such authorities as Lord Kelvin, Dr. Lodge, and Mr. O. Heaviside in the matter.

The Discussion on Mr. Sutherland's paper "*The Laws of Molecular Force*," was re-opened by Prof. PERRY reading a communication from the President, Prof. FITZGERALD.

He objected to discontinuous theories, especially when Clausius had given a continuous formula much more accurate over a very long range than Mr. Sutherland's discontinuous one. The introduction of Brownian motions without carefully estimating the rates required and energy represented, and without giving any dynamical explanation of their existence, was not satisfactory. It would, he said, be most interesting if Mr. Sutherland would calculate the law of variation of temperature with height of a column of convectionless gas, under conduction alone (for Maxwell thought the inverse fifth power law of molecular attraction was the only one that gave uniformity of temperature under these conditions), and if necessary make tests with solid bars. Referring to the statement that molecular attraction at 1 c.m. was comparable with gravitation at the same distance, he thought Mr. Boys would question this, and he suggested an *experimentum crucis* of the inverse fourth power law. Both the inverse fourth and inverse fifth power laws assumed symmetry which did not exist. He also took exception to other parts of the paper.

Dr. GLADSTONE, referring to the relative dynic and refraction equivalents given in Table XXVIII. of the paper, said he thought it interesting to make a similar comparison between dynic and dispersion, and magnetic rotation equivalents. The result as exhibited in a complete table showed a certain proportionality between the four columns, but the differences were beyond the limits of experimental error. Mr. Sutherland, however, sometimes reckoned the dynic equivalent of hydrogen as 0.215 and at other times looked upon it as negligible. The analogies between the optical equivalents did not depend on the proportionality of the numbers so much as upon the fact that the refraction, dispersion, and magnetic rotation equivalents of a compound was the sum of the corresponding equivalents of its constituent atoms, modified to some extent by the way in which they were combined. Whilst a somewhat similar relation held true for the dynic equivalents, the effect of "double-linking" of carbon atoms, so evident in the optical properties, was scarcely perceptible. The result of calculating the constants from M^1 instead of from M^2 was next discussed, the effect of which was to quite upset the proportionality before noticeable.

Mr. S. H. BURBURY said that on referring to the author's original paper on which the present one was based, he found that uniform distribution of molecules was assumed. On this supposition the demonstrations given were quite correct, and the potential was a maximum. If, however, the molecules were in motion, the average potential must be less than the maximum, and the deductions in the present paper being based on wrong assumptions were liable to error.

Prof. RAMSAY remarked that many statements in the paper on the subject of critical points were very doubtful. Separate equations for the different states of matter were not satisfactory, neither was the artificial division of substances into five classes. The predicted differences in the critical points due to capillarity had not been found to exist. Speaking of the virial equation, he said that hitherto R had been taken as constant. Considerations he had recently made led him to believe that R was

not constant. The whole question should be reconsidered regarding R as a variable.

Mr. MACFARLANE GRAY said he had been working at subjects similar to those dealt with in Mr. Sutherland's paper, but from an opposite point of view, no attraction being supposed to exist between molecules. In the theoretical treatment of steam he found that no arbitrary constants were required, for all could be determined thermodynamically. The calculated results were in perfect accord with M. Cailliet's exhaustive experiments except at very high pressures, and even here the theoretical volume was the mean between those obtained experimentally by Cailliet and Battelli respectively.

Prof. HERSCHHEL pointed out that Villard's equation of the virial, where the chemical and mechanical energies were not supposed to balance each other. Mr. Sutherland's paper all turns on the existence of such a balance, and he (Prof. Herschel) could not understand why this balancing was necessary.

The Discussion was then closed and the meeting adjourned.

NOTICES OF BOOKS.

Outlines of Organic Chemistry. By CLEMENT J. LEAPER, F.C.S. London: Iliffe and Son. Small 8vo., pp. 118.

WE had begun to hope that the stretch of elementary chemical treatises with which we have been inundated for so many years was beginning to abate; it seems we were mistaken. "Still they come," and the painful questions which they suggest remain without an answer. We know that if a man becomes really interested in any Science he requires in after life, perhaps, ten times as many books on the subject as he did when a pupil.

Now, as no such supply of advanced chemical works seems to be demanded, we can only conclude that of the multitudes who have attended chemical classes and been duly examined, a vast majority at once throw the study aside and in after life remain unaffected by what they have learnt. This fact, a peculiarity, we believe, of Britain—might alone suffice to show that as far as higher education is concerned we are "on the wrong tack."

This little work before us is avowedly examinational, and of course duly "departmental."

The Pharmacy and Poison Laws of the United Kingdom. Their History and Interpretation. With a brief Account of the Pharmacy Laws in Force in Australasia, Canada, and Cape Colony. London: Office of the Chemist and Druggist. Melbourne: Office of the Chemist and Druggist of Australasia.

IF the poison and pharmacy laws of this country were free from inconsistency they would be grossly un-English. It seems almost farcical to hedge in the sale of "poisons" with complicated formalities, whilst the open sale of explosives, ammunition, and fire-arms is allowed to go on. This is the greater grievance, since the lawful and harmless uses of fire-arms are very limited, whilst the lawful and harmless uses of poisons in the arts and manufactures are almost innumerable.

We know that there are persons who seek for an extension of the present laws, and would even restrict the sale of the ordinary mineral acids to the chemists and druggists. Several attempts have been in fact made in this direction, but fortunately for the arts they have not been successful. The Council of the Pharmaceutical Society in 1882 made itself responsible for an attempt of this nature.

The work before us, it will be seen, is simply historical and declaratory. It neither criticises nor justifies the existing laws, nor does it advocate their alteration. It

will be very useful to all dealers in chemicals as explaining to them in clear language what articles they may sell and under what regulations.

Short Manual of Experimental Chemistry. By A. DUPRÉ, Ph.D., F.R.S., F.C.S., &c., and H. WILSON HARRIS, Ph.D., F.C.S., &c. Second Edition, Revised. London: C. Griffin and Co., Limited.

THIS work is an exceedingly favourable specimen of—as we may call them—the intermediate class of chemical text-books. It is distinct, on the one hand, from the bald manuals whose existence we have so often had to regret, and, on the other hand, from the necessarily voluminous publications of Watts, or of Roscoe and Schorlemmer. Whilst useful as a class-book it may often be advantageously consulted as a work of reference. Among its many commendable features it is free from the taint of examinationalism.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 19, November 7, 1892.

Honours to M. Pasteur.—The members of the Section of Medicine and Surgery have formed themselves into a committee to present some appropriate testimonial to M. Pasteur on the occasion of his reaching the age of 70 years, which will take place on December 27th.

The Influence of the Distribution of Manures in the Soil upon their Utilisation.—Th. Schlösing.—The author is studying the effects of a complete and uniform distribution of manures in the soil, a point which, he considers, has not met with due attention. As the three essential principles of manures he regards potash, nitrogen, and phosphoric acid. His results will be given in a future communication.

Note on M. Berthelot's Reply to his Paper of October 24th.—Th. Schlösing.—The author declines to reply to the personalities of M. Berthelot.

Attempt at a General Method of Chemical Synthesis.—Raoul Piçet.—(See p. 262).

The Rotatory Power of the Salts of the Diamines.—Albert Colson.—All the salts examined were deflected in the same direction as the generating acid. If we extend to stable salts the principle of the conservation of the molecular type, we understand that one and the same solvent without immediate action upon the acid or the salts will not alter the direction of the rotatory power. We shall consider it natural that the tartrates, e.g., are dextrorotatory in an aqueous solution like the generating acid, whilst the diacetyl tartrates are levorotatory under the same conditions and from the same cause.

Volumetric Determination of the Alkaloids.—E. Léger.—Referring to the claim of priority raised on this subject by Herr Harsten as against M. Barthe, the author claims the priority for himself on the evidence of a note published in the *Journ. Phys. Chem.*, vol. xi., p. 425 (1885), on the application of phenolphthalein to volumetric analysis.

The Fixation of Free Nitrogen in Plants.—Th. Schlösing, junr., and Em. Laurent.—The authors contend that whilst the lower plants are capable of fixing the free nitrogen of the atmosphere it remains in them after fixation, whilst the subjacent soil is not enriched. In their experiments the fixation was effected by a

mixture of mosses and algae, doubtless accompanied by bacteria. Consequently the process is confined to the surface, instead of taking place, as according to M. Berthelot, in the lower beds of the soil.

Observations on the above Paper.—M. Duclaux.

Observations on the Foregoing Papers.—M. Berthelot.—This controversy promises to become tedious.

On γ -Achromoglobine—A New Respiratory Globuline.—Dr. A. B. Griffiths.—The author gives to this new globuline the remarkable formula $C_{72}H_{915}N_{194}SO_{183}$.

Bulletin de la Société Chimique de Paris.

Series 3, Vols. vii. and viii., Nos. 17 and 18.

Action of Chlorine upon the Alcohols of the Fatty Series. Isobutylic Alcohol.—A. Brochet.—The author has obtained a chlorine derivative of isobutylic acid of the composition C_4H_7ClO . It is a colourless mobile liquid of a pungent but bitter taste. It burns with a sooty flame bordered with green. It is evidently an aldehyd. Its boiling-point is 90° , and its specific gravity = 1.053.

Derivatives of α -Naphthylacetylene and β -Naphthylacetylene.—J. A. Le Roy.—The author describes diphthaloyl, naphthylpropionic acid. He further gives an account of the action of chlorine upon α -ethyl-naphthalene, the formation of α -naphthylacetylene; the action of phosphorus perchloride upon β -methyl-naphthylketone; β -naphthylacetylene, and of its hydration.

Process of the Oxidation and Sulphonation of Organic Substances by Ammonium Bisulphate.—Marcel Lachaud and Ch. Lepierre.—On causing pure aniline to act upon the bisulphate and heating the mass for a sufficient time it darkens and becomes black. In this mass the authors have recognised and partially separated by dialysis a black amorphous body soluble in water but insoluble in alcohol, a violet and a blue substance. If the impure aniline of commerce is caused to react upon ammonium bisulphate it turns red at once; on continuing to heat it passes through violets and blues to black. An entire series of colours, probably novel, are thus formed between 200° and 350° . Some of them are soluble in amylic alcohol (acid or ammoniacal), such as the reds and the violets. The blues and the blacks are insoluble. Some of them are strongly fluorescent.

On Paradiethylbenzene.—H. Fournier.—The author has undertaken to study the bromo-derivatives of paradiethylbenzene in the lateral chains.

On Benzylpentaethylbenzene.—H. Fournier.—This substance, $C_{23}H_{32}$, boils without decomposition above 360° . It crystallises from alcohol in fine white needles, which melt at 88° – 89° . It is very soluble in benzene, even in the cold, in ether, and boiling alcohol; but it is very sparingly soluble in cold alcohol.

Specific Gravity of Silk.—Leo Vignon.—The author contends that the values obtained by M. de Chardonnet are too high, as his silks must have been more or less weighted with metallic elements.

Thermochemical Study of Certain Organic Substances with Mixed Functions.—Leo Vignon.—Not adapted for useful abstraction.

Revue Universelle des Mines et de la Metallurgie.

Vol. xix., No. 3, September 1892.

Transformation of the Ordinary Safety-lamp into a Sensitive Indicator of Fire-damp.—F. Clowes.—A paper communicated to the Royal Society.

Royal Institution. — Christmas Lectures. — Sir Robert Ball, F.R.S., will deliver a course of six lectures (adapted to a juvenile auditory) on "Astronomy," commencing on Tuesday, December 27.

MEETINGS FOR THE WEEK.

MONDAY, 28th.—Society of Arts, 8. (Cantor Lectures). "The Generation of Light from Coal-Gas," by Prof. Vivian B. Lewes. Medical, 8.30.

TUESDAY, 29th.—Institute of Civil Engineers, 8.

WEDNESDAY, 30th.—Society of Arts, 8. "The Copper Resources of the United States," by James Douglas. British Astronomical Association, 5. Royal, 4. (Anniversary).

THURSDAY, Dec. 1st.—Institute of Electrical Engineers, 8.

Geologists' Association, 8.

Quekett Club, 8.

Chemical Society, 8. "On the Formation of Orcinol and other Condensation Products from Dehydracetic Acid," by J. Norman Collie. "Isolation of Two Predicted Hydrates of Nitric Acid," by S. U. Pickering. "Anhydrous Oxalic Acid," by W. W. Fisher. "Observations on the Origin of Colour and of Fluorescence," by W. N. Hartley. "The Origin of Colour—Azobenzene," by H. E. Armstrong. "The Reduction Products of α , α -Dimethyl- α , α -Diethylpentane," by Dr. Kipping. "The Products of the Action of Sulphuric Acid on Camphor," by Dr. Armstrong and Kipping. "Methods of Showing the Spectra of Easily Volatile and their Salts, and of Separating their Spectra from those of the Alkaline Earths," by W. N. Hartley.

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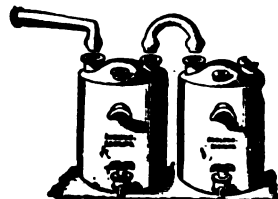
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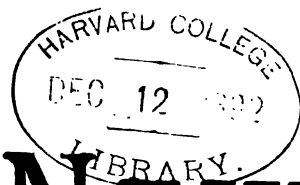
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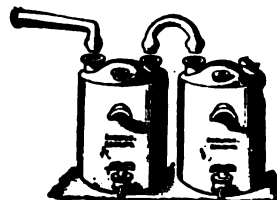
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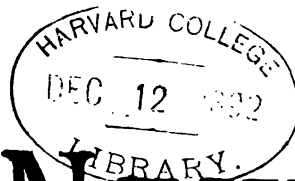
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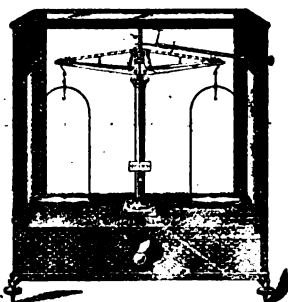
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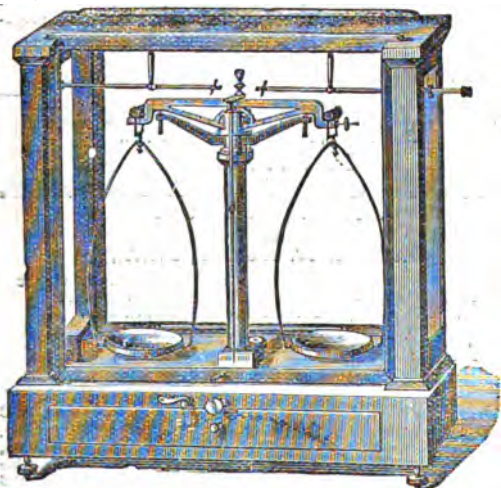


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THE CHEMICAL NEWS.

VOL. LXVI., No. 1723.

ON THE ACTION OF PHOSPHINE ON SELENIUM DIOXIDE.*

By SIR CHARLES A. CAMERON.

THE author has studied the action of dry phosphine gas on a solution of selenium dioxide in absolute alcohol. Complete absorption takes place, and a rich yellow precipitate appears. The attempts made to determine accurately the composition of the yellow compound failed owing to its instability, for it no sooner made its appearance than it began to turn red owing to separation of selenium. It was found to contain both phosphorus and selenium, but at each determination in different proportions. Attempts to retard decomposition by conducting the processes in such a way as to exclude atmospheric air, and to expose the yellow compound to low temperatures, proved of little use. It was found that the proportion of selenium thrown out of solution varied according to temperature, and to the rapidity with which the phosphine was transmitted through the alcoholic solution. The greater part of the selenium remained in the alcohol, and exercising a reducing action on the alcohol produced ethyl selenide, $(C_2H_5)_2Se$.

DETECTION OF GOLD IN DILUTE SOLUTIONS.

By T. K. ROSE, B.Sc.,
Assistant Assayer to the Royal Mint.

It is well known that if large quantities of boiling water are poured into a solution of stannous chloride, a yellowish white gelatinous precipitate of tin hydrate is obtained. If the water contains a little chloride of gold the precipitate is coloured red (purple of Cassius). A solution of one part of gold per million parts of water treated in this way gives a bright rose-coloured precipitate almost instantaneously in a small test-tube. One in four millions gives a paler colour easily detected in a test-tube if comparison is made with the precipitate caused by distilled water. For more dilute solutions a greater bulk of liquid is required, and the precipitation is best effected in beakers.

If 0.0000311 grm. gold (one-millionth of an oz. troy) is dissolved in 3.11 litres of water, and the solution, containing one part per hundred millions, is raised to boiling and poured suddenly into a large beaker containing 10 c.c. of a saturated solution of $SnCl_2$ in water acidulated by HCl so as to mix the two liquids as rapidly as possible, a bluish purple precipitate is obtained. This precipitate, when collected in a test-tube, differs markedly in colour from a precipitate obtained by pure water in the same way. There seems no reason why a still more dilute solution of gold should not yield a colour if precautions are taken to ensure the complete mixture of precipitant and solution.

Quantitative results based on comparison may also be obtained with care, as the precipitates are quite stable in water. The presence of NaCl (3 per cent), $CaSO_4$, KCl, KBr, NH_4Cl , a little free HCl, &c., or all of these, do not interfere with the reaction. The precipitate is soluble in ammonia and is re-precipitated, showing its original colour, on neutralising with HCl. Synthetically prepared

sea-water containing gold to the amount of one in twenty millions (three-quarters grain per ton) is equally sensitive, but the colour is in this case a blackish rather than a purple violet. I am proceeding to test real sea-water in the same way, though quantitative results cannot be expected, since Sonstadt states (CHEMICAL NEWS, xxvi., p. 159) that only a small portion of the gold present is precipitated by stannous chloride.

This modification of a very well-known test appears likely to be useful in chlorination mills, where it is often desirable to detect the presence of gold in liquids containing as little as 1 in 5,000,000. The most dilute solution that reacts if treated in the ordinary way by $SnCl_2$ is one per million (*vide* text books, *passim*), and then only after a lapse of some hours.

Royal Mint, Nov. 26, 1892.

A SIMPLE CHEMICAL EXPERIMENT.

By ALEXANDER JOHNSTONE.

As illustrating a lecture on oxygen or air, a strong solution of pyrogallol in KHO or NaHO is often exposed to the gas or the atmosphere to show its great power of absorbing free oxygen, and its instant change of colour when exposed to it. This experiment "tells better" if a clear colourless solution of alkaline pyrogallol be shown to the class before exposure to oxygen. This can be done very easily and quickly. Into a rather deep test-glass, such as is ordinarily used in lecture experiments, place some solid pyrogallol acid and then a little water, just enough to barely dissolve it. Next put a small handful of sodium carbonate into a flask and cover with HCl to drive the CO_2 off. Pour the CO_2 gas into the glass above the pyrogallol, and then add the KHO to the latter. The class will see that the alkaline solution below the CO_2 remains colourless. To show the change caused by the presence of O, pass the latter from a tube into the lower stratum of the CO_2 covering, or incline the glass so as to throw out the CO_2 and admit the air. The change will be instantaneous.

This experiment should also be of service in making evident to the eye the diffusion of gases—the heavier CO_2 —slowly mixing upwards with the air and the latter downwards with the CO_2 , as evinced by the assumption of colour by the pyrogallate, and the gradual deepening of the colouration as the diffusion progresses.

Queen Margaret's College, Glasgow,
Nov. 18, 1892.

ON THE ORIGIN OF THE VARIOUS COLOURS OF NITRIC ACID.

By L. MARCHLEWSKI, Ph.D.

It is well known that on adding a little water to fuming nitric acid of a brown tint it immediately assumes a green colour, which, on further addition of water, turns blue, and on still further dilution entirely disappears.

This phenomenon was explained by Péligot, who relied principally on the physical properties, especially the colouring powers of the oxides of nitrogen assumed to be present. The explanation is briefly this:—That brown fuming nitric acid owes its colour to the nitrogen tetroxide dissolved in it, which possess the well-known ruddy-brown colour; that the green acid contains a mixture of brown nitrogen tetroxide and blue nitrogen trioxide along with nitric acid, and lastly, that the blue solution contains a mixture of nitric acid and nitrous acid, the colour being due to the nitrogen trioxide present. Nothing further was stated concerning the condition of

* Abstract of a Paper presented to the Royal Dublin Society Nov. 16, 1892.

the oxides N_2O_4 and N_2O_3 ; i.e., it remained uncertain whether free N_2O_4 is to be regarded as existing in the solution as such, and whether N_2O_3 exists as the free oxide or the acid.

The last question could not be settled at that time, as nothing was definitely known as to the existence of a hydrate of nitrous acid. It appeared to me that the above explanation, which could only be regarded as an *a priori* one, was unsatisfactory and required confirmation by experiment.

I made a series of experiments, the first part of which was published in the *Berichte* of the German Chemical Society. This paper was critically discussed by Veley in the *CHEMICAL NEWS*, lxi., 175. His remarks place my researches on the subject of this paper in a false light. My original method of research was as follows (*Berichte*, xxiv., 3271).

A stream of carbon dioxide was passed through each of the differently coloured acids, and the oxides evolved absorbed in concentrated sulphuric acid. According to Lunge (*Ber.*, 1882, p. 438) nitrous anhydride is absorbed to form pure nitrososulphuric acid and nitrogen tetroxide to form a mixture of nitrososulphuric acid and nitric acid. The analysis of the nitrogenous bodies with regard to (a) the total nitrogen, and (b) the nitrogen existing as nitrous acid, by Lunge's excellent method, ("Alkali-maker's Pocket-Book," Lunge and Hurter), should give information with regard to the oxides evolved from the coloured acids, and thus, as I thought, furnish a clue to the cause of colouration.

Mr. Veley censures me for not having mentioned in my communication either the time during which CO_2 was allowed to act on the acids, or the temperature at which the experiments were carried out. He remarks on the absence of any statement with regard to drying the gases, as well as any attempt to check the results by examination of the decolourised acids. Moreover, he makes me state that Péligot's explanation should be set aside as absolutely incorrect.

I am driven to conclude from Mr. Veley's statements (1) that he has only read my first communication hurriedly; (2) that he has not read my second paper at all; and (3) that he suggests the carrying out of useless experiments. The method of research used in the first paper depends, as already mentioned, on the mechanical removal of oxides of nitrogen by means of a stream of carbon dioxide and the analysis of the nitroso bodies carried away and absorbed in sulphuric acid. I expressly mentioned that each acid was treated with carbon dioxide until completely decolourised. The time varied with the amount of acid to be decolourised; the determination of the duration of the experiment would then have no object. Concerning the temperature I expressed myself with sufficient precision on p. 3273 (*Berichte*, xxiv.), where the decolourisation is said to have taken place in the cold.

I did not incline to believe in any particular influence of the temperature on the reaction, because, according to Péligot's theory, the only colour-producing oxides are N_2O_4 and N_2O_3 , and by raising the temperature the first would only split up into two molecules of NO_2 , and the second into NO_2 and NO , which latter behave exactly like nitrous acid in the presence of sulphuric acid. A rise of temperature would then cause absolutely no change in the analytical result except for the possible volatilisation of nitric acids. The CO_2 must obviously be dried before using, for a dilution of the prepared acid would alter its composition.

It is evident that the gas after passing through the coloured acid will be charged with water vapour, as well as with oxides of nitrogen; this circumstance can, however, have no influence on the analysis, as the amount of dilution necessary to decompose the nitrous acids is not nearly reached.

The result of my first research was to prove that the analytical methods used by me showed no difference in the composition of the green and blue acids. I observed

at the same time (*Berichte*, xxiv., p. 3275) that nitric oxide appears along with the higher oxides, and promised to report further on the occurrence of this gas.

By the prosecution of this question I became convinced that the analytical method which I had originally used was inadequate; that the nitric oxide observed was not necessarily present as such or in loose combination with other bodies, but that it can also be formed by the spontaneous decomposition of an aqueous solution of nitrous acid.

Montemartini (*Zeit. Physik. Chemie*, 1891, p. 93), maintained that this decomposition proceeds according to the differential equation for chemical reactions of the first order, and further, although this requires confirmation, that the rate of decomposition of nitrous acid, in presence of nitric acid, diminishes with increased concentration of the latter (*Atti Della Reale Accad. dei Lincei Redic.*, i., p. 63—67).

My supposition has been confirmed (*Zeit. Anorgan. Chemie*, i., p. 374); it can be proved that a stream of CO_2 passed through an aqueous solution of nitrous acid carries off a considerable quantity of nitric oxide. The problem as to the constitution of the coloured acids could not, therefore, be carried out in the way described. If the nitric oxide is produced by the splitting up of nitrous acid it masks the fact—thanks to its property of reacting with nitrogen tetroxide in the presence of sulphuric acid in the same way that N_2O_3 does.

If, on the contrary, nitric oxide is generated from some other source, or really does play a chemical part in the colouration of the acids, my earlier experiments would not prove decisive when placed alongside experiments instituted with aqueous solutions of nitrous acid. Consequently I felt justified in my second communication (*Zeit. Anorgan. Chemie*, i., 377) in drawing the conclusion that the physical theory completely expresses all the facts known; for I proved (1) that in the most highly concentrated fuming nitric acid of a brown colour, only nitrogen tetroxide exists along with nitric acid, and (2) that by dilution of such acid with ice-cold water, no loss of nitric oxide took place.

Now since, as is generally known, N_2O_4 can only split up into nitrous and nitric acids by the action of either water, sulphuric acid, or the alkalis, we must conclude that the mixture formed by dilution of brown fuming nitric acid can only contain HNO_3 , N_2O_3 , and N_2O_4 (the green acids), or HNO_3 and N_2O_3 (the blue acids).

The imputation that I deny Péligot's views is, then, entirely unfounded. I do not, of course, assume that N_2O_4 exists as such in the brown acid, I believe that I have furnished more reasons for the assumption that it combines chemically with the nitric acid (*Zeit. Anorgan. Chemie*, i., p. 380). The form in which N_2O_3 exists in the blue solution is quite unknown; we cannot unfortunately adopt any definite view with regard to it, since it has never been proved what the blue aqueous solutions of N_2O_3 may represent, whether they are simply solutions of N_2O_3 , i.e., N_2O_3 molecules distributed through a definite space by means of the solvent medium, or whether they are solutions of the hydrate HNO_2 .

I attacked this question, narrowed by the following consideration:—If N_2O_3 is present as such in an aqueous solution, the solution cannot be a conductor of electricity; if it is a conductor a decomposition must take place, and this would consist in the formation of the ions H and NOO (as $2NO$ and O). The necessary experiments were, however, so surrounded with difficulties that they gave somewhat indefinite results, and I determined not to publish them.

Mr. Veley censures me, lastly, for not having analysed the residual acids. That, as a matter of fact, I did not do, and why? In a third article (*Zeit. Anorgan. Chemie*, ii., p. 18), called forth by a research of Montemartini (*Atti Della Reale Accad. Lincei Redic.*, i., 63—67), I proved that a combination of the analysis of the gases evolved, with the analysis of the residual acids, can only

lead to illusory results, against which I wished to guard myself.

There is, unfortunately, no exact quantitative method of separating the oxides NO , N_2O_3 , and N_2O_4 , and nitric acid when all are present in the same solution.

The general results of all considerations lead more and more to the conviction that, so long as the chemistry of the individual oxides of nitrogen makes no further progress, it will remain impossible to find a direct experimental solution to the question of the constitution of blue and green nitric acids.

Every criticism of my work is welcome, particularly when it concerns such an extremely difficult subject as the chemistry of the oxides of nitrogen. They must, however, fulfil one condition: the critic must not pick out a single contribution—not even the first one—expressly designated as an introduction, and treat it alone to a close inspection.

The critic should rather have before him the whole of the work done in that province by the person criticised, and if he be an inorganic chemist he should not overlook a journal which is entirely devoted to inorganic chemistry, viz., "Die Zeitschrift für Anorganische Chemie von Kruss." These conditions Mr. Veley has not fulfilled.

Dr. Schunck's Laboratory,
Manchester.

ATTEMPT AT A GENERAL METHOD OF CHEMICAL SYNTHESIS.

By RAOUL PICTET.

THE first point which we have had to verify experimentally in order to prove the agreement of our fundamental hypothesis with facts, consists in demonstrating that at very low temperatures all chemical reaction ceases. We have made more than two hundred experiments to this end, in which we have brought in contact the substances which react most energetically, those whose reactions are the most conspicuous, and those, lastly, which are in the liquid state notwithstanding the greatest cold.

We relate here only some of these observations:—

1. Concentrated sulphuric acid at 89 per cent, and that with ten molecules of water, having 35 per cent, yield two liquids, the congealing points of which are -56° for the former and 88° for the latter.

We put at -125° congealed sulphuric acid in contact with caustic soda finely pulverised and likewise refrigerated to -125° in a capsule. On strongly compressing the acid into the powder of caustic soda there appeared no reaction.

We then introduced into the refrigerating tank two insulated wires, between which we caused the spark of a powerful Ruhmkorff's coil to strike over. We found that the frozen sulphuric acid conducted the spark very well, and after a quarter of an hour's operation we saw that the reaction of the acid upon the alkali was effected on the paths of the sparks, but without extending to the adjoining parts. The weight of sodium sulphate is thus relatively trifling, and this product is sprinkled over the surface of the column of frozen sulphuric acid. The temperature shown by the thermometer in the centre of this column of frozen acid, at the end of fifteen minutes is -121° , whilst the contents of the refrigerating tank were kept at -145° . These facts having been established, we withdrew the tube from the refrigerating tank, so as to allow the temperature to rise gradually. About -80° the reaction suddenly took place in mass, breaking the tube in consequence of the abrupt change of temperature.

Dilute sulphuric acid at 31 per cent behaved exactly in the same manner.

2. *Sulphuric Acid and Caustic Potassa.*—The operation was effected exactly in the same manner as with soda,

and gave the same results, only the reaction in mass took place already at -90° .

3. *Sulphuric Acid and Concentrated Ammonia.*—No reaction above -80° . A limited reaction under the influence of the electric spark, then at -65° or -60° a reaction in mass with a sudden rise of temperature.

4. *Sulphuric Acid and Sodium Chloride.*—No reaction below -50° ; from -50° to -25° limited reaction; then above, a reaction in mass.

5. *Sulphuric Acid and Calcium Sodium Carbonates.*—Taking sulphuric acid at 35 per cent liquid at -80° , no reaction with these two carbonates. The first bubbles of carbonic acid were liberated only at -56° for sodium carbonate and at -52° for calcium carbonate. At -15° with marble, and at -30° with sodium carbonate the action is turbulent. All other carbonates behave essentially in the same manner.

6. *Nitric Acid with the same Substances as with Sulphuric Acid.*—The acid is cooled down to -125° , as well as all the substances with which it is brought into contact. With caustic potassa and soda the reactions are at first null, but they are developed some degrees lower than with sulphuric acid if the temperature is allowed to rise gradually outside the tank.

With sodium chloride the reaction begins already at -74° with the aid of the spark.

7. *Metallic Sodium at 84 per Cent.*—The alcohol is cooled down (liquid) to -78° with the sodium. If the sodium is thrown into the alcohol there is no reaction. It begins only about -48° , and is suddenly developed in mass.

8. *Sodium and Sulphuric Acid at 35 per Cent.*—Both cooled down to -85° and brought into contact—no reaction. About -50° the reaction appears suddenly with flames. Below -50° sodium in contact with the acid retains its metallic lustre, as it does in dilute alcohol.

9. *Potassium* acts like sodium; at -68° (instead of -50°) it spontaneously ignites the hydrogen liberated by the sulphuric acid at 35 per cent ($\text{SO}_4\text{H}_2 + 10\text{H}_2\text{O}$).

10. We have made some experiments on reactions which yield solid precipitates.

Sulphuric Acid and Barium Chloride.—We refrigerate separately sulphuric acid at -85° and a solution of barium chloride in alcohol. We mix the two liquids, adding a few crystals of barium chloride. No reaction can be perceived and the sulphuric acid remains transparent. The precipitate only appears at -70° . At -40° the reaction is complete.

Hydrochloric Acid and Silver Nitrate.—An alcoholic solution of silver nitrate is cooled to -125° , as is also hydrochloric acid at 33 per cent. On mixing the liquids there is seen no deposit or turbidity. At -90° the reaction appears slightly, and it is complete at -80° .

11. *Caustic Potassa and Phenolphthalein.*—The potassa is dissolved in alcohol and the phenolphthalein likewise. They are cooled separately down to -135° , the pasty state. On mixing there is no reaction. The temperature is allowed to rise, and at -100° the red tint appears, and at -80° the colour is intense.

Litmus with Sulphuric Acid and Hydrochloric Acid.—An alcoholic solution of litmus is cooled down to -140° , and poured either into frozen sulphuric acid or upon liquid hydrochloric acid at -125° . The solution remains blue indefinitely at -120° in spite of frequent agitation. At -110° the solution suddenly turns red with hydrochloric acid, and at -105° with sulphuric acid.

Summary.

We may sum up as follows the researches made in this direction:—

1. At the temperatures comprised between -155° and -125° we have not been able to recognise any chemical reaction whatever were the bodies brought into contact.

2. The visible reactions, such as the effect of acids upon tincture of litmus, &c., are produced at lower tempera-

tures than other very energetic reactions, such, e.g., as that of metallic sodium upon sulphuric acid.

3. In all chemical reactions we may find two phases, according to the temperature at which we operate.

A. The *slow reaction* which is produced below a certain limit of temperature which is special for the substances brought into contact. This reaction is manifested under the influence of the electric spark, according to the distance between the actual temperature and such limit of temperature.

B. The *reaction in mass*, in which the rise of temperature produced by the portions which react communicates to the adjacent parts heat enough to make them react.

In most cases to obtain and keep up the slow reaction, we must remove by radiation the heat developed by the combination; otherwise the temperature very quickly reaches the limit of the *reaction in mass*.

4. The electric spark seems to be the best excitant to provoke *slow reaction*.

5. It is therefore experimentally shown that every chemical reaction always commences with a *period of negative energy*, in which work must be supplied to the components from without, to permit their combination. The chemical work, called by M. Berthelot preliminary or preparatory, is therefore a general fact in nature.—*Comptes Rendus*, cxv., p. 814.

THE ELECTROLYSIS OF METALLIC FORMATES.*

By HILL SLOANE WARWICK.

(Continued from p. 267).

I. Influence of Dilution upon the Precipitation of Cadmium.

Cadmium taken. Grm.	Cadmium deposited. Grm.	H ₂ O. C.c.	Free acid. C.c.	Time. Hours.	OH gas per minute. C.c.
1. 0.0994	—	100	none	$\frac{1}{2}$	1.75
2. 0.0497	—	100	"	$\frac{1}{2}$	1.75
3. 0.0994	—	100	0.5	$\frac{1}{2}$	1.75
4. 0.0994	0.0218	100	5	1	1.75
5. 0.0497	0.0109	100	$\frac{1}{2}$	1	1.75
6. 0.0248	0.0053	100	$\frac{1}{2}$	1	1.75
7. 0.0124	0.0026	100	$\frac{1}{2}$	1	1.75
8. 0.0062	0.0011	100	$\frac{1}{2}$	1	1.75

In 1 and 2 no free acid was added, and in 3 only 0.5 c.c. was present; all three were failures. The amount of acid was then increased to 5 c.c. and the experiment repeated, all the other conditions remaining the same. The deposit was adherent and compact. The poles were 3.16 c.m. apart, and had an area of (2.85 c.m. $\times$ 3.8 c.m.) $\times$ 2.

II. Influence of Temperature upon the Precipitation of Cadmium.

Cadmium taken. Grm.	Cadmium found. Grm.	H ₂ O. C.c.	Free acid. C.c.	H ₂ O gas per minute. C.c.	Temperature in deg. C.
1. 0.1231	0.0240	150	10	1.75	20°
2. 0.1231	—	150	10	1.75	40°
3. 0.0497	0.0088	145	25	1.75	20°
4. 0.0497	0.0110	145	25	1.75	40°
5. 0.0497	0.0210	145	25	1.75	60°
6. 0.0497	0.0257	145	25	1.75	80°

2 was very spongy, and was covered with a white gelatinous deposit resembling cadmium hydrate. The amount of cadmium was then diminished more than half, while the amount of formic acid present was increased to 25 c.c. 5 and 6 were somewhat spongy, but adherent. The increase was:—20°—40° 0.0022 grm., 40°—60° 0.0100

grm., 60°—80° 0.0047 grm. The amount of metal deposited increased with rise of temperature, being greatest at 80°, but the greatest ratio of increase was at 60°, being almost five times greater than at 40°, and more than twice as great as at 80°. These results were so different from those obtained with copper that a second series of determinations was made, in which the amount of cadmium in the solution was reduced still more in order to ensure a compact deposit at the higher temperatures. The results, which were in close accord with those above, are as follows:—

Cadmium taken. Grm.	Cadmium deposited. Grm.	H ₂ O. C.c.	Free acid. C.c.	OH gas per minute. C.c.	Temperature in deg. C.
1. 0.0198	0.0022	135	15	1.25	20°
2. 0.0198	0.0031	135	15	1.25	40°
3. 0.0198	0.0078	135	15	1.25	60°
4. 0.0198	0.0102	135	15	1.25	80°

III. The Influence of Pole Separation upon the Precipitation of Cadmium.

Cadmium present. Grm.	Cadmium deposited. Grm.	H ₂ O. C.c.	OH gas per minute. C.c.	Separation of electrodes. C.m.
1. 0.0994	—	700	2.2	1.58
2. 0.0994	0.0059	700	1.25	1.58
3. 0.0994	0.0023	700	0.8	1.58
4. 0.0994	0.0009	700	0.8	3.16
5. 0.0994	0.0002	700	0.8	6.33
6. 0.0994	—	700	0.8	12.66

Although 20 c.c. of free formic acid was present in 1 and 2, both were failures, the latter, though it was weighed, being merely approximate, some particles having been washed off. The current was then reduced to 0.8 c.c. HO gas per minute. Adherent deposits were obtained, but in such small quantity that 5 yielded only a trace. The ratio of diminution was:—3—4 0.0014 grm., 4—5 0.0007 grm. Area of electrodes (3.8 c.m. $\times$ 3.48 c.m.) $\times$ 2, time one hour, free acid present present 10 c.c.

I. Influence of Dilution upon the Precipitation of Zinc.

Zinc present. Grm.	Zinc deposited. Grm.	H ₂ O. C.c.	Free acid. C.c.	OH gas per minute. C.c.
1. 0.1250	0.0300	100	0.5	1.75
2. 0.0625	0.0155	100	0.25	1.75
3. 0.1250	0.0173	100	5	1.75
4. 0.0625	0.0083	100	$\frac{1}{2}$	1.75
5. 0.0313	0.0043	100	$\frac{1}{2}$	1.75
6. 0.0156	0.0028	100	$\frac{1}{2}$	1.75

1, 2, 5, and 6 were spongy, especially the last. Distance between the poles 3.16 c.m. Area (2.85 c.m. $\times$ 3.8 c.m.) $\times$ 2, time one hour.

II. Influence of Temperature upon the Precipitation of Zinc.

Zinc taken. Grm.	Zinc deposited. Grm.	H ₂ O. C.c.	Free acid. C.c.	OH gas per minute. C.c.	Temperature in deg. C.
1. 0.1539	—	150	10	0.3	20°
2. 0.1026	0.0145	150	10	1.8	20°
3. 0.1026	—	150	10	1.8	40°
4. 0.0205	—	150	none	0.3	20°
5. 0.0205	—	150	"	0.8	20°
6. 0.0205	—	150	"	1.3	20°
7. 0.0513	0.0029	145	5	0.9	20°
8. 0.0513	0.0019	145	5	0.9	40°
9. 0.0513	0.0010	145	5	0.9	60°
10. 0.0513	—	145	5	0.9	80°
11. 0.0513	—	145	5	0.9	80°
12. 0.0513	—	145	none	0.9	80°

1, 3, 5, and 6 were very spongy. In 4, 10, and 11 no deposition of metal took place; 12 was spongy and was covered with a white coating of zinc hydrate. At 80° no

* Read before the American Philosophical Society, November 6, 1891. From the *Proceedings of the American Philosophical Society*, xlix., No. 136.

metal was deposited in the presence of free acid, provided the current was not too strong. The ratio of decrease with rise of temperature was:—20—40° 10 grms., 40—60° 9 grms., 60—80° no deposit. The distance between the poles was 2·85 c.m. Area of electrodes (3·8 c.m. × 3·16 c.m.) × 2. Duration of experiment one hour.

III. Influence of Pole Separation upon the Precipitation of Zinc.

Zinc taken. Grm.	Zinc deposited. Grm.	Free acid. C.c.	H ₂ O. C.c.	OH gas per minute. C.c.	Time. Hours.	Distance between poles. C.m.
1. 0·0102	0·0046	10	700	1·9	3	1·58
2. 0·0102	0·0023	10	700	1·9	3	3·16
3. 0·0102	0·0015	10	700	1·9	3	6·33
4. 0·0102	0·0003	10	700	1·9	3	12·66

Area of electrodes (3·8 c.m. × 3·48 c.m.) × 2. The deposit was firm and compact. Compared with the results obtained with copper and cadmium, the result in 4 is too low.

Lead (Determined Electrolytically).

On account of tendency of lead and manganese to separate in the form of peroxide at the positive pole, it was deemed advisable to make a series of experiments on the metals themselves before attempting to effect their separation. The results were as follows:—

Lead taken. Grm.	Lead found. Grm.	Free acid. C.c.	H ₂ O. C.c.	OH gas per minute. C.c.	Time. Hours.	Difference from theory.
1. 0·1153	—	5	100	1	16	—
2. 0·1153	—	20	100	1·2	48	—
3. 0·1153	—	5	100	2·8	3	—
4. 0·1153	—	20	100	2·8	16	—

Fifty c.c. of a lead formate solution were used in each of the above experiments. In all of them the lead was deposited in a spongy state at the cathode with more or less peroxide on the positive pole.

As the moist metal deposited on the cathode rapidly oxidises, even when adherent and compact, the results obtained are invariably too high, and in practice it is customary to estimate lead as peroxide on the anode, securing its deposition in that form by the addition of nitric acid to the solution. The results obtained with free formic acid, as given above, were not such as to justify attempting its separation from either copper, cadmium, or zinc.

Manganese (Determined Electrolytically).

Manganese taken. Grm.	Manganese found. Grm.	Free acid. C.c.	H ₂ O. C.c.	OH gas per minute. C.c.	Time. Hrs.	Difference from theory. Percentage.
1. 0·0554	0·0552	5	100	2·2	17	—0·36
2. 0·0554	0·0556	5	100	2·7	18	+0·36
3. 0·1108	0·1101	20	100	2·8	24	—0·63
4. 0·0554	—	30	100	1·6	16	—

The platinum dish was made the anode, the wire spiral serving as the negative pole. With small quantities of free acid, 1 and 2, considerable peroxide of manganese separated on both poles; with larger quantities (3, 4) only very slight traces were found on the cathode. The deposition in 4 was not complete. The peroxide formed a black lustrous coating on the dish, adherent while moist, but scaling off upon being heated.

The manganese which separated on the cathode was removed by means of a small piece of filter paper, which was ignited and the ash added to the contents of the dish, which was then raised to an intense heat in order to convert the peroxide of manganese into Mn₂O₃, in which form it was finally weighed. Traces of Mn were found in solution 3.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 17th, 1892.

Sir HENRY ROSCOE, M.P., F.R.S., Vice-President, in the Chair.

ON taking the Chair, Sir HENRY ROSCOE congratulated the Fellows on the very great improvement effected in the Society's rooms, especially in the meeting room, during the recess.

The Treasurer, Professor THORPE, agreed with the Chairman in thinking that the fellows present had good reason to congratulate themselves on the changed conditions under which they met. The meeting room had undergone, as they saw, what was practically complete reconstruction, the position of the table and of the seats having been altered, with the result that not only had a very considerable air-space been gained, which would tend to the better ventilation of the room, but also additional accommodation, both in actual seating space and in the means of entrance and exit, had been secured. Provision had been made for a larger supply of fresh air and for the removal of that which passed into the rooms. Moreover, it would be noticed that the electric light had been substituted for gas as an illuminant throughout the building; this, it was hoped, would promote the comfort of Fellows attending the meetings, not only in its effect on the nature of the air within the rooms, on the cleanliness of the apartments, and on the preservation of their decorative character, but also by affording greater facilities for the exhibition of specimens, diagrams, and lantern projections. It would be understood that the structural and other alterations required by these changes necessarily occupied a considerable time, and although every effort had been made to complete the changes within the recess, it had been considered desirable to postpone the date of the opening meeting to a week or so later than the usual time, in order to secure everything being in proper working order when the Society met. The structural alterations had been planned and their execution superintended by Mr. Martin L. Saunders, to whom the thanks of the Society were due for the care and assiduity with which he had discharged the duty he undertook. These alterations had been made by Messrs. Colls and Son, who had also carried out the re-decoration of the whole of the apartments to the entire satisfaction of the Committee. The installation of the electric lighting was planned by Professor Ayrton, to whom the Society was under a very special obligation for the great amount of time, thought, and energy he had expended on the work. The business of wiring the building and of affixing the fittings was entrusted to Messrs. Spagnoletti and Crookes, with the result that all present were able to enjoy. The fittings, that is, brackets and pendants, were supplied by Messrs. Faraday and Sons, and do credit to the reputation of that firm for artistic work. Experience could alone show how these various alterations would work in practice, but enough had been seen already to indicate that they were undoubtedly great improvements, and would conduce to the health and comfort of the Fellows.

On the motion of the Chairman, seconded by the Treasurer, it was resolved: That the best thanks of the Fellows be tendered to Mr. Martin L. Saunders and Professor Ayrton for their valuable services.

Certificates were read for the first time in favour of Messrs. Robert Samuel Adcock, Rio Tinto Mines, Huelva, Spain; William Smellie Anderson, Marine Station, Granton; David Avery, Queen's College, Melbourne University, Australia; Arthur John Bensusan, 13, Lansdown Road, Kensington Park, W., and Darling Point, Sydney; Horace Vincent Butfield, 16, Thistlewaite

Road, Clapton, N.E.; Frederick Walter Carlton, Marlow House, Swindon; Ernest Victor Clark, 5, Tisbury Road, West Brighton; Arthur James Cooper, The Schoolhouse, Bromyard, Herefordshire; Andrew William Craig, 77, Peel Street, North Melbourne; Joseph R. Denison, 1, Park View Terrace, Manningham, Bradford; Thomas Duxbury, Richmond Terrace, Darwen; Martin Onslow Forster, 32, Binfield Road, Clapham Road, S.W.; William French, 74, Walmersley Road, Bury, Lancashire; Walter Goodall, Alma House, Pudsey, near Leeds; John Goodfellow, F.R.M.S., 2, Rutland Terrace, High Road, Leyton, Essex; Thomas Gray, 16, Craigmore Terrace, Downanhill, Glasgow; William Thomas Gronow, Port Pirie Smelting Works, Port Pirie, South Australia; Walter S. Haines, Chicago, U.S.A.; James G. Hardy, 1, Keir Terrace, Pollokshields, Glasgow; Samuel C. Hooker, Philadelphia, U.S.A.; John Horsfall, 88, Scar Terrace, Bacup, Lancashire; Edgar Edward C. Horwill, 104, Ferndale Road, Clapham, S.W.; W. H. Ince, Ph.D., 12, Cowley Street, Dean's Yard, Westminster; John F. V. Isaac, 18, Montserrat Road, Putney, S.W.; John Jackson, Rhymney; Samuel Jackson, Nether Thong, Huddersfield; William George Johnson, 4, Hilgrove Road, Finchley Road, Hampstead, N.W.; K. K. Kacker, Delhi, India; Thomas Torrens Knowles, School House, Lancaster; G. Krause, Cöthen (Anhalt, Germany); Thornton Charles Lamb, Polygon, Ardwick, Manchester; William Howard Lloyd, 5, Belmont Villas, New Walk, Leicester; Arnold G. Maddox, 15, Fleetwood Street, Clissold Park, N.; Colin Francis Moorwood, 260, Barnsley Road, Sheffield; J. B. Nickolls, 8, Colledge Terrace, Grange, Guernsey; Hugh Ramage, Royal College of Science, Dublin; James Wyllie Rodger, 76, Anerley Park, S.E.; Norman Scott Rudolf, Sewan Sarun, Bengal, India; Satyaprasad Sarbadhicary, 53, Wellington Street, Calcutta; Augustus Schloesser, Ph.D., M.Sc., 7, Victoria Crescent, Busby, Near Glasgow; William James Sell, 1, Bene't Place, Cambridge; George Arthur Shaw, 112, Bramhall Lane, Stockport; Reginald des Foyes Shepherd, 6, Coleman Street, Hull; Charles Spackman, Sibley, Loughborough; Ernst Speidal, B.S., 17, Quincey Street, Chicago, Illinois; A. H. Turton, Ashley, Carlisle Road, Edgbaston; Frederick William Westaway, 1, Aytoun Road, Stockwell, S.W.; John Lowe Whiteside, 51, Canon Street, Bolton; Frederick Henry Wigham, 25, Pinderfield Road, Wakefield; William Williams, Smithfield Street, Dolgelly, N. Wales; N. T. M. Wilmshire, Altona, Orrony Road, Elsternwick, Melbourne.

The CHAIRMAN announced that the following Address had been forwarded to the sister society in Berlin;—

Address to the Deutsche Chemische Gesellschaft.

The Chemical Society of London desires to offer its warmest congratulations to the Deutsche chemische Gesellschaft on the occasion of the celebration of its Twenty-fifth Anniversary; while, at the same time, it joins with the Sister Society in deploring most deeply the recent irreparable loss of one who was long so intimately associated with both bodies,—who exercised so important an influence on their development, and who took so large a share in the guidance of the affairs, first of the one and then of the other.

The Chemical Society of London is proud to think that it may properly regard the German Society as its direct lineal descendant through Hofmann. No offspring could possibly have done greater credit to its parent; indeed, the rapidity of growth and youthful vigour of the offshoot is beyond all precedent. A true mirror of the progress of chemical science, the stately series of volumes issued by the Society during the first quarter-century of its existence, will ever serve as the priceless historical record of the marvellous advance of chemistry during the period; and that advance would appear to be in no small degree due to the incitement afforded to experimental inquiry by the regular and frequent issue of the now far-famed *Berichte*.

But probably it will in the future come to be regarded as the greatest service of the Deutsche chemische Gesellschaft that it has done so much to render possible the ultimate denationalisation of chemical science. Chemists of all nations record their results in the pages of its publication, which has become a meeting ground where international jealousies disappear and the spirit of utmost toleration prevails. No one more clearly recognised the greatness of such a service than Hofmann. In 1863, when President of the Chemical Society of London, speaking at the Twenty-second Anniversary Meeting of the delivery of lectures to the Society by distinguished foreign chemists, he said: "The Chemical Society has loudly proclaimed the cosmopolitan character of science, and that henceforth it will look upon the several nations engaged in scientific pursuits as upon so many federal members of a great Republic united by the love of science, and pledged by contributions to a common treasury, as it were, to uphold its cause and to raise its dignity." The cosmopolitan influence of the great moving spirit of its councils during the first twenty-five years of the existence of the Deutsche chemische Gesellschaft will ever be regarded as a priceless service rendered to chemical science by Hofmann.

The following resolution was passed at the meeting of the Council in the afternoon:—

"The Council learns with deep regret that, through the death of Dr. Longstaff, on the 23rd September last, the Society has lost its senior Fellow and one of its founders. The deep interest which Dr. Longstaff took in the Society, and in the promotion of the interests of chemical science, having been evinced by the munificent gift which secured the establishment of the Research Fund, his name will ever remain associated with the history of the Society, and will be retained fresh in the memory of the Fellows through the triennial award, to those who have distinguished themselves in chemical research, of the Medal bearing his name."

The following papers were read:—

63. "*Fluosulphonic Acid*." By T. E. THORPE, F.R.S., and WALTER KIRMAN.

The authors have prepared this compound by distilling a slight excess of hydrogen fluoride into a weighed platinum flask containing a known amount of sulphuric anhydride, both the condensing tube and the receiver being surrounded with a mixture of ice and calcium chloride; the excess of hydrogen fluoride was subsequently removed by passing a current of dry carbon dioxide through the liquid product at a temperature between 25° and 35°. The interaction is attended with the development of much heat.

Fluosulphonic acid, SO_3HF , is a thin colourless liquid boiling with slight decomposition (apparently into SO_2F_2 and SO_4H_2) at 162.6°, which, it is noteworthy, is a higher temperature than that at which chlorosulphonic acid boils (155.3°). It has but little action on the dry skin, feeling greasy to the touch, and being without the intense blistering action of hydrogen fluoride.

DISCUSSION.

Professor RAMSAY expressed the opinion that the name fluosulphonic acid was preferable to fluosulphonic acid.

Mr. PAGE and also Sir HENRY ROSCOE asked whether the isolation of fluorine had been confirmed by any independent observer since the announcement of Moissan's discovery.

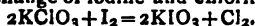
Dr. ARMSTRONG said the fact that fluosulphonic acid had a higher boiling point than chlorosulphonic was of special interest, as in the case of corresponding "atomic" compounds the fluorine compound, as a rule, had a lower boiling point than the chlorine compound; he thought that on the whole the evidence favoured the view that chlorosulphonic acid was a so-called molecular compound, and, perhaps, an explanation was to be found in this

direction. He suggested also that probably the fluor- and chlor-acids would be found to yield the pyrofluoride and pyrochloride, and not the sulphuryl compounds on distillation.

Professor THORPE, in reply, said that he had no special views with regard to the use of the syllable fluor instead of fluo. He had spent considerable time in attempting to repeat Moissan's work, without obtaining definite results; but possibly he had not had the good fortune to hit on the precise experimental conditions requisite for success. He had, however, given Moissan a long account of his trials without obtaining any specific information from him in reply.

64. "Note on the Interaction of Iodine and Potassium Chlorate." By T. E. THORPE, F.R.S., and GEORGE H. PERRY.

The interaction is usually represented by the equation $3\text{KClO}_3 + \text{I}_2 = \text{KClO}_4 + \text{KCl} + \text{KIO}_3 + \text{ICl} + \text{O}_2$; the authors find, however, that it primarily and in the main involves a simple interchange of iodine and chlorine:—



When care is taken in heating the mixture, it is possible to convert practically the whole of the iodine present into potassium iodate, the equivalent amount of gaseous chlorine being liberated.

65. "The Magnetic Rotation of Sulphuric and Nitric Acids, and of their Aqueous Solutions; also of Solutions of Sodium Sulphate and Lithium Nitrate." By W. H. PERKIN, Ph.D. F.R.S.

The author has previously shown that, although the molecular rotations of the fatty acids and their ammonium salts are not appreciably influenced by the presence of water, yet that of sulphuric acid is to a considerable extent, the rotation rapidly falling for small dilutions, but diminishing as the amount of water is increased; in these experiments the examination was only extended to a mixture corresponding to $\text{H}_2\text{SO}_4 + 3\text{OH}_2$. Nitric acid was also found to behave in a similar manner.

On account of remarks by Professor Ostwald on these results, and the interest which is taken in the subject of solutions, a more extended series of observations has been undertaken. The results are given in the paper in a tabular form, and are also represented graphically. In the case of sulphuric acid and sodium sulphate it is shown that there is no apparent connection between the value for the rotation and extent to which dissociation is supposed to take place, down to solutions containing about 9 per cent of acid or 12 per cent of sodium sulphate. The same conclusion was come to from the examination of solutions of these substances at temperatures of about 90°, when the rotation increased instead of diminishing, as it should have done, according to the dissociation hypothesis. The results, however, are not inconsistent with the assumption that combination takes place with the formation of $(\text{HO})_2\text{SO}_4$.

The results obtained with nitric acid give a different kind of curve to that afforded by sulphuric acid, viz., one consisting of a practically straight line down to solutions containing about 33 per cent of HNO_3 , after which it appears to curve somewhat downwards; and, although it does not deviate so much as sulphuric acid from that representing the dissociation, yet it does not correspond at all closely with it. It is considered that these results may indicate the formation of a compound resulting from the union of the acid with water, e.g., $(\text{HO})_3\text{NO}$.

Lithium nitrate resembles nitric acid in its behaviour. The rotations of the haloid hydrides in aqueous solution are also referred to, showing that as those of the concentrated solutions at first change very rapidly with small dilutions, but more slowly with large dilutions, at last becoming nearly stationary, they are not in agreement with their dissociation, which increases with dilution.

66. "Note on the Refractive Indices and Magnetic Rotations of Sulphuric Acid Solutions." By S. U. PICKERING.

The values for the refractive indices of these solutions obtained by van der Willigen when plotted out and examined by a flexible lath, show the existence of a well-marked "break" as well as a maximum at 84.5 per cent (the monohydrate), another "break" at 57.7 per cent (the tetrahydrate), and another at 24—30 per cent. The first two of these agree with the breaks shown by the magnetic rotations, and all three of them agree with breaks found in the examination of other properties. The experimental points available were not sufficiently numerous to indicate more than the most prominent "breaks," and it was found that the densities when treated so as to lead to the indications of the most prominent "breaks" only, indicated these same three. For this purpose the molecular volumes were calculated from the densities of solutions of the same strength as those used by Dr. Perkin, and when plotted out they showed "breaks" at 83.5, 60, and about 30 per cent. When the same number of values, but for solutions of different strengths, were taken, the same "breaks" were still indicated.

DISCUSSION.

Professor RAMSAY drew attention to a work by van der Waals, on the *continuity* of the liquid and gaseous states, the fundamental equation underlying all the calculations in which is—

$$p = \frac{RT}{(v-b)} - \frac{a}{v^2}.$$

This expression, graphically interpreted, gives a curve of double flexure, with very abrupt changes of curvatures, provided numbers be appropriately chosen. (The curve was drawn on the blackboard.) He entirely dissented from Mr. Pickering's conclusions as regards "breaks," and denied the existence of anything but continuous transitions from one state to another; and he maintained that it was no more sensible to attempt to detect "breaks" with a bent lath than to assume that all curves were parabolas or circles.

Dr. WALKER drew attention to the circumstance that in calculating the amount of electrolytic dissociation from the electrical conductivity of mixtures of sulphuric acid and water, Dr. Perkin had neglected to take account of one of the factors which determine the conductivity, namely the speed of the ions, which is intimately connected with the viscosity of the solutions. His "dissociation" curves, therefore, did not represent at all the actual degree of dissociation in the strong solutions studied by him, for in them the viscosity is comparatively great. The same objection applied to the temperature experiments. The great increase of conductivity caused by elevation of temperature is due almost exclusively to the increased speed of the ions, and not to any change in the dissociation. In his opinion, therefore, the conclusions drawn by Dr. Perkin as to the want of concordance between his results and the theory of electrolytic dissociation were from this cause invalid.

Mr. PICKERING, in reply to Professor Ramsay, said that, as he had long ago pointed out, there were, of course, many classes of curves which were not amenable to treatment with a flexible lath; the fact that Prof. Ramsay was able to instance one of these neither proved nor disproved anything.

67. "The Hydrate Theory of Solutions. Some Compounds of the Alkylamines with Water." By S. U. PICKERING.

In making a series of determinations of the freezing-points of solutions of these amines, it was found that most of them formed one or more definite crystalline hydrates. Sixteen amines were examined, of which two were entirely and two very sparingly soluble, and twenty-four hydrates in all were isolated. Hydrates with the same number of water molecules occur in many different cases, but no connection could be traced between the degree of hydration and the nature of the amine. Indications of hydrates were also obtained by "breaks" in

the curves representing the freezing-points, and in every instance but one a hydrate of the composition thus indicated in the case of one amine was actually isolated in the crystalline condition in the case of some other amine. The lowest hydrate isolated (in four cases) contained $\frac{1}{2}\text{H}_2\text{O}$, and the highest $11\text{H}_2\text{O}$. The freezing-points of the hydrates ranged from $+5^\circ$ to -71° . In the case of the amines themselves, as well as of such hydrates as contain the same number of water molecules, the freezing points seem to fall as the number of carbon atoms present in the alkyl radicle increase, and to rise as the number of radicles in the amine increases. The following is a list of analysed hydrates isolated as crystals:—

$\text{EtNH}_2, 5\text{H}_2\text{O}$,	$\text{EtNH}_2, 5\cdot5\text{H}_2\text{O}$,
$\text{PrNH}_2, 5\text{H}_2\text{O}$,	$\text{BaNH}_2(\text{iso-}), 7\text{H}_2\text{O}$,
$\text{Et}_2\text{NH}, 5\text{H}_2\text{O}$,	$\text{Me}_2\text{NH}, 7\text{H}_2\text{O}$,
$\text{Pr}_2\text{NH}, 5\text{H}_2\text{O}$,	$\text{PrNH}_2(\text{iso-}), 8\text{H}_2\text{O}$,
$\text{Me}_2\text{NH}, 8\text{H}_2\text{O}$,	$\text{PrNH}_2, 8\text{H}_2\text{O}$,
$\text{Et}_3\text{N}, 2\text{H}_2\text{O}$,	$\text{Et}_2\text{NH}, 8\text{H}_2\text{O}$,
$\text{Me}_3\text{N}, 3\text{H}_2\text{O}$,	$\text{Me}_3\text{N}, 11\text{H}_2\text{O}$.

DISCUSSION.

Professor THORPE, after referring to the fact that the late Professor Guthrie had investigated the relationship of certain of the alkylamines to water as far back as 1884 (*Phil. Mag., Proc. Phys. Soc.*, 1884, 169), said that among other things Guthrie had pointed out that while a mixture of triethylamine and water containing from 15 to 50 per cent of the alkylamine was clear and transparent at ordinary temperature, on warming it became suddenly turbid owing, apparently, to the triethylamine being thrown out of solution. On cooling the liquid it again became clear, but could again be rendered turbid on warming. The temperature at which this change occurs is remarkably constant, viz., about $18\cdot4^\circ$. In this behaviour a solution of triethylamine in water resembles an aqueous solution of ammonia. It occurred to the speaker to try whether the effect of pressure on the solution would be to increase the apparent solubility of the alkylamine in water by observing whether the turbidity would disappear under pressure, the temperature being maintained above $18\cdot4^\circ$. Experiments showed that this was the case. By enclosing a quantity of the solution in a Cailletet tube, to which pressure could be applied in the ordinary way by the Ducrest pump, it was found that on rendering the liquid turbid by surrounding the tube with tepid water, the turbidity almost instantly disappeared when the pressure was increased a few atmospheres, and as quickly reappeared on releasing the pressure. Professor THORPE proceeded to demonstrate this phenomenon with the aid of the electric light by throwing an image of the tube on the screen. On gently warming the tube the solution became so turbid as to practically stop the passage of the light. On applying pressure, the solution was seen to clarify, but on releasing the pressure it again became milky, and, in fact, nearly opaque.

68. "The Atomic Weight of Boron." By EMILY ASTON, B.Sc. (Lond.), and WILLIAM RAMSAY, Ph.D., F.R.S.

An account is given of the re-determination of the atomic weight of boron by two methods: by the determination of the water of crystallisation in borax, and by the conversion of anhydrous sodium borate into sodium chloride by distillation of the borax with chlorhydric acid and methyl alcohol, and weighing the resulting sodium chloride.

The aggregate of seven experiments in which 42 grms. of borax were deprived of water gave as atomic weight $10\cdot921$, with a probable error of $0\cdot01$.

Two series of experiments were made in which borax was converted into sodium chloride. The first series, in which over 20 grms. were employed, gave as atomic weight $10\cdot942$; the second series, in which more than 23 grms. were converted, gave as atomic weight $10\cdot966$. The result of the second series is regarded as more probably correct.

The authors discuss the discrepancy between their results and Abrahall's (*Chem. Soc. Trans.*, 1892, 650) and give reasons why they regard the value deduced by this observer ($10\cdot825$) as too low; they think that his boron bromide may have been contaminated with hydrogen bromide present as $\text{BBr}_3\cdot\text{HBr}$.

69. "Methoxyamido-1:3-Dimethylbenzene and Some of its Derivatives." By W. R. HODGKINSON and LEONARD LIMPACH.

Having devised a method of separating 1:2:4-metaxylidine from paraxylidine, &c., with which it is mixed in commercial xylidine, the authors have had the opportunity of preparing 1:2:4-metaxylenol in large quantity. An almost theoretical yield of this phenol was obtained by diazotising a solution containing only 5 per cent of the xylidine sulphate and then steam distilling; the product did not solidify even at -20° , but a considerable quantity was caused to crystallise by adding solid, obtained by cooling a small portion by means of carbon dioxide and ether. The presence of a trace of water was found to prevent crystallisation. On nitration, metaxylenol yields almost the theoretical amount of a nitroxylenol, in which the NO_2 group is contiguous to the hydroxyl. The authors have prepared the corresponding amido- and hydroxy-xylenols and their methylated derivatives (dimethylanisols); they also describe a quinaldine derivative, formed by condensation from the methoxy-amidoxylenol and ethylic acetoacetate.

Extra Meeting, December 13th.

An Extra Meeting of the Society will be held on Tuesday, December 13th, at 8 p.m., the Anniversary of the death of Stas. A paper, specially prepared for the occasion by Professor J. W. MALLET, F.R.S., entitled "Jean Servais Stas, and the Measurement of the Relative Masses of the Atoms of the Chemical Elements," will be read and discussed.

PHYSICAL SOCIETY.

Ordinary Meeting, November 25th, 1892.

Prof. S. P. THOMPSON, D.Sc., F.R.S., Vice-President, in the Chair.

MESSRS. T. J. Fry, A. G. Bessemer, junr., and E. T. Fournier d'Abbe were elected Members.

The following communication was made:—

"Experiments in Electric and Magnetic Fields: Constant and Varying." By MESSRS. RIMINGTON and WYTHE SMITH.

In the first set of experiments shown, exhausted electroless tubes and bulbs were rotated rapidly in a constant electric field between two parallel charged discs. Double fan-shaped images were produced by the tubes, due to the displacement currents which pass to equalise the potentials at the ends of the tubes. These fans were not symmetrical with respect to the lines of electric force, but were displaced in the direction of rotation. In explanation of this phenomenon it was pointed out that as a tube rotated, the potential difference between its ends increased until this difference was sufficient to break down the dielectric in the tube. The discharges would therefore pass at the ends of the intervals during which the difference of potential was rising, and consequently the images would be displaced from the symmetrical position in the direction of rotation. The number of discharges produced during one revolution was found to depend on the strength of the electric field, but not on the speed of rotation, and that end of the tube which was approaching the negatively charged plate appeared brightest. These experiments were referred to as examples of the direct conversion of mechanical energy into light. Instead of rotating tubes in a constant electric field the tubes were next kept stationary, and a varying electric field produced

by connecting the plates with an influence machine allowed to spark; under these conditions the tubes and bulbs were seen to glow. Using large suspended plates charged by an induction coil, long tubes were caused to glow brightly even at considerable distances away from the plates. The glow could be apparently wiped out by passing the hand along the tube.

Another series of experiments were performed in varying magnetic fields. With a view to showing Hertzian phenomena to large audiences the authors tried Geissler tubes to replace the spark gap in resonators with great success. When large Leyden jar circuits were used, the effects were very brilliant. Another form of resonator consisted of a bent wire terminating in two plates, between which an exhausted tube was placed. This tube became luminous when the resonator was placed in the vicinity of a fairly large Hertz oscillator.

Other experiments similar to those shown before the Society at Cambridge by Prof. J. Thomson, on discharges in exhausted bulbs were then made, the bulbs being placed with a coil of wire of four turns, forming the connection between the outer coatings of two small jars, whilst sparks passed between knobs connected with the inner coatings. The bulbs glowed brightly at each discharge, rings of light being seen near their inner surfaces. On putting a ring tube outside the coil this was also seen to glow. The most brilliant part of the glow always occurred in close proximity to the wire coil.

A secondary coil, wound by the side of the above-mentioned primary, could be short-circuited at will; this had the effect of decreasing or extinguishing the luminosity in the bulb or tube. Bright sparks passed between the secondary terminals when held a short distance apart, but the shock experienced by touching the ends was not serious.

The above arrangement, with the addition of two Geissler tubes placed in series between the outer coatings of the jars, was used to illustrate the fact that closing the secondary diminishes the impedance of the primary circuit of a transformer.

Experiments on condensers made of tin-foil on glass were shown. In one of them, parts of the coatings in the form of letters had been removed, and the spaces became luminous when the condenser was connected with an induction coil. In another experiment a glass plate was moved to and from a condenser, and a musical note could be heard whose pitch increased as the distance between the glass plates diminished. The note was said to be the octave of an open organ pipe whose length was equal to the distance between the plates.

Mr. SWINBURNE thought some of the effects shown were not Hertzian, but merely cases of ordinary mutual induction. He enquired whether the vacuum tubes would still glow if the Leyden jars were removed from the so-called resonating circuits. He was also of opinion that in the magnetic experiments the surfaces of the bulb, and not the enclosed gases, took the charges.

Mr. WATSON asked if the authors had tried screening off the long waves by a wet cloth. If the effects still existed this would prove that they were Hertzian.

Mr. BLAKESLEY wished to know if the images of the rotating tubes were at equal angular distances.

Mr. SMITH pointed out that these distances were not equal, but corresponded to equal changes of potential.

Prof. AYRTON remarked that the only cases where the materials of the bulbs, tubes, &c., did not influence the results were those in which discharges were produced by varying magnetic fields.

Mr. E. T. CARTER thought an induction coil a more efficient machine for producing the glow in tubes than the alternator, &c., used by Mr. Tesla.

Mr. TROTTER asked if the authors had observed whether the glow produced by passing a discharge through a wire wound in a long pitch spiral round a tube formed an open or a closed circuit of light.

Prof. S. P. THOMPSON said he first noticed that sparks

passed between pieces of metal in the vicinity of an induction coil sparking into a condenser in 1876, when he was showing some experiments on telegraphic apparatus before the Society, but unfortunately he did not pursue the subject. Long before Mr. Tesla's investigations Dr. Bottomley had shown that exhausted tubes could be caused to glow, but it was not until Tesla produced such phenomena on a large scale that people recognised how much light could be got in that way.

Mr. RIMINGTON, in replying to a question by Professor Thompson, said the notes heard when the glass plate approached the condenser were of very high pitch. The explanation, why in the experiments performed in varying magnetic fields the bright parts of the luminous discharges were near the wire, appeared to be that the E.M.F. was greatest in these places. Although he had not tried the experiment suggested by Mr. Swinburne of taking off the Leyden jar, he felt sure that doing so would stop the glow.

NOTICES OF BOOKS.

Lightning Conductors and Lightning Guards. A Treatise on the Protection of Buildings, of Telegraph Instruments and Submarine Cables, and of Electric Installations generally, from Damage by Atmospheric Disturbances. By OLIVER J. LODGE, D.Sc., F.R.S., LL.D., M.I.E.E., Professor of Physics in University College, Liverpool. London: Whittaker and Co., and G. Bell and Son.

In this work it is very fully shown that the possible mischief of a lightning flash is resolvable into two elements: (1) its disruptive or explosive violence; and (2) its heat. The former effect is most to be dreaded when the flash is well conducted except at a few places, and the latter when it encounters great resistance. In Britain a thunder-storm is generally accompanied with a third kind of mischief more to be dreaded than the ignition of houses or the destruction of a few men or cattle: the weather is too generally upset for at least a week—a loss which in the midst of our brief summer is tantamount to an impaired harvest. But whether the wave of cold is the cause or the effect of the electric action, it is an evil for which our electricians see at present no remedy. Dr. Lodge points out that leading the charge to earth does not always get rid of it, as it may rise again until the energy is consumed.

The present ideas—perhaps we might better say those of a time but recently past—concerning electric conductors are shown to be in many respects defective, and as sometimes leading to undesirable results. Lightning has strange vagaries against which it is not always possible to provide. Everything which projects upwards should be spiked, but very high rods do not appear desirable. For the conducting rods, iron, though less perfectly conductive than copper, is preferred, chiefly because it is much less likely to be stolen. Says Dr. Lodge:—"Let the lightning come to you; do not go to meet it. Protect all your ridges and pinnacles, not merely the highest, and you will be safer than if you built yourself a factory chimney to support your conductor upon. At present the immediate neighbourhood of a factory chimney or a steeple is not a safeguard, but a source of mild danger even when itself thoroughly protected. If it have no conductor, it is no doubt still more dangerous."

Dr. Lodge recommends that metal gutters, balconies, &c., should be connected at both ends. Lead water-pipes and gas-piping inside a house should not be connected.

The system recommended by Clerk Maxwell is totally different. He seeks to enclose a house, or still more a magazine in a stout wire cage.

It is a remarkable and unpleasant fact that the Hôtel de Ville at Brussels, the most perfectly and elaborately

protected building in the world, the masterpiece of M. Melsens, has been struck and set on fire.

Contrary to received ideas, lightning has been known to penetrate into a railway tunnel, into coal mines, into cavities surrounded by high buildings with leaden roofs, iron water-pipes, and iron portculis, to get at a steel gas bracket. The insulation, or attempted insulation, of conductors is condemned on the faith of actual observation.

Dr. Lodge has, by the publication of this work, done good service to all who require lightning conductors or have to fit up these protectors.

Explosives and their Powers. Translated and Condensed from the French of M. BERTHELOT by C. NAPIER HAKE, F.I.C., Inspector of Explosives to the Government of Victoria; and WILLIAM MACNAB, F.I.C. With a Preface by Lieut.-Colonel J. P. CUNDILL, R.A., H.M. Inspector of Explosives. With Illustrations. London: John Murray, 1892.

THIS elaborate work is not, like, *e.g.*, that of Eissler, a practical treatise on the manufacture, the analysis, and the uses of the various explosives now known. Its central idea is the application to the study of explosives of thermo-chemistry, well known as the speciality of M. Berthelot. Setting out from this basis, the author expounds the general properties of explosives, those features upon which their efficacy depends.

The author considers that explosive substances are characterised by the sudden development of a considerable expansive force, by which means they effect enormous mechanical work. Such work, however, it must be admitted, is mainly of a destructive character. The "unspeakable advantage" due to the replacement of the old war appliances has its fearful set-off in the facilities which the so-called high explosives now offer to the criminal and the conspirator.

In the action of explosives two orders of effects have to be distinguished: the one due to pressure, and the other to the work developed, or, practically speaking, to the heat liberated. Here attention is called to the fact that the products developed at the moment of the explosion are not necessarily the same as those found after cooling. The heat liberated is calculated from our examination of the products of the reaction, though a part of this heat is transformed into work. The pressure exerted is calculated from the volume of gas liberated. The duration of the transformation is an important characteristic of an explosive. It is found that nitro-glycerin and gun-cotton explode in a quite different manner, according to the manner of their ignition. They may burn away quietly or they may exert violent shattering effects. The latter result occurs chiefly when mercury fulminate is used as a primer.

It is, of course, impossible to enter into the details of this work; but there is one statement which we can notice only with profound regret. M. Berthelot writes:—"The explosion which happened in 1871 in the Stowmarket factory, and in which twenty-four persons perished, was attributed, rightly or wrongly, to imperfect supervision." The verdict of the jury, founded on the unanimous evidence of the scientific experts called, was that a portion of the gun-cotton had been tampered with after the manufacturing process was completed. This conclusion was reached alike by the chemists representing the Home Office, the War Department, and the Gun-cotton Company. Nor, as we well remember, could the facts admit of any other possible interpretation.

If we set this one unfortunate passage aside, the work will be of the highest value to manufacturers of explosives.

On Certain Crystalline Sodium Titanates.—H. Cormimboeuf.—Sodium sesquitanate has the composition $3\text{TiO}_3 \cdot 2\text{NaO}$; the sodium bititanate is $2\text{TiO}_2 \cdot \text{NaO}$; the trititanate is $3\text{TiO}_2 \cdot \text{NaO}$.—*Comp. Rend.*, cxv., No. 20.

CORRESPONDENCE.

THE CHARTER OF THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—It is pretty well known amongst the Members of the Institute of Chemistry, that for some considerable time past the Council has been engaged in considering a scheme for the re-arrangement of the system of examinations at present adopted in reference to admission to the Institute, and that unexpected difficulties have arisen through the nature of the wording of the Charter. As originally drafted, a principal feature in the proposed new system was substantially the carrying into effect of the views of the writer put before the Institute Conference, held in May, 1891, as regards the necessity for further extending the examinational system. At present, this only deals with what may be conveniently termed the *preliminary scientific* training of the candidate, and does not embrace any adequate testing of the nature and extent of the *professional training* acquired subsequently to duly laying the foundations of his scientific education.

Obviously, to render the possession of the Fellowship of the Institute of Chemistry a guarantee of competency "to practise in analytical chemistry, and to advise in technological chemistry" (to quote from the Charter), the tests of competency hitherto applied require considerable extension; if the Institute is to issue a certificate implying that the holder thereof has been found to possess proper qualifications so to practise and advise, it must thoroughly sift and test the attainments of each candidate in at least some one branch of analytical chemistry as employed in professional practice, or of technological chemistry: *i.e.*, the proficiency of each candidate in the branch selected by him must be ascertained and duly authenticated; so that he would take his Fellowship in, for example, the branch of metallurgical chemistry, or in that of the manufacture of dyeing materials and their employment in dyeing textile fabrics, or in that of food and drug analysis, &c.

It is evident from the wording of the Petition presented to H.M., praying that a charter should be granted, that the object sought was the empowering of the Institute to grant *certificates of professional competency* to such persons as should be found duly qualified to hold them. This clearly results from the above quotation and the following ones (the italics are the writer's). "The Society aims at the elevation of the profession of consulting and analytical chemistry, and the promotion of the efficiency and usefulness of persons practising the same, by compelling the observance of strict rules of membership, and by setting up a *high standard of scientific and practical proficiency*." "It would greatly promote the objects for which the said Institute has been instituted, and would also be for the public benefit, if the members thereof were incorporated by Royal Charter with power to afford facilities for the *better education and examination* of persons desirous of qualifying themselves to be *public and technical analysts* and *chemical advisers* in scientific subjects of public importance, and with power to grant such *certificates of competency*."

The present system of examinations certainly tests more or less satisfactorily the candidate's knowledge of general theoretical chemistry and various allied subjects, as well as of the ordinary kinds of laboratory manipulations and processes taught in a college laboratory of the usual type; *i.e.*, it tests his possession of a fairly sound foundation on which the superstructure of professional acquirements may be subsequently raised. This is good as far as it goes, but it falls a long way short of thoroughly carrying out the objects aimed at by the petitioners and by the founders of the original Institute of Chemistry previously incorporated: because the passing of examinations of the kind hitherto conducted affords no adequate guarantee of ability, without further special training, to

practise analytical chemistry as met with professionally (e.g., in the laboratory of a works or of a public analyst), or of competency to advise in technological chemistry or in scientific subjects of public importance; whereas the avowed object of the petitioners was to obtain power to grant certificates which should be such a guarantee, founded on the having given proof of possessing the requisite knowledge and experience.

It is perfectly true that there are very great difficulties indeed in the way of accurately ascertaining the strictly professional qualifications of candidates, apart from their scholastic attainments; i.e., in gauging the extent of their further knowledge of chemistry as applied to arts and manufactures and the wants of the general public, acquired *after* leaving the training college, or having otherwise obtained the requisite preliminary scientific education. But it is equally true that the object set forth by the petitioners in seeking a Charter was substantially to attempt to overcome these difficulties, and ensure that the possession of the Fellowship of the Institute of Chemistry should be of itself an attestation of professional competence,—a result hitherto not attained to any notable extent, wherefore the attempts of the Council to improve matters in this respect.

It might naturally be supposed that when a Royal Charter has been applied for to enable the petitioners to do certain things, and has been duly granted in consequence, the document would be so worded as at least to convey the idea that the powers prayed for have been actually conferred; but as regards the Charter of the Institute of Chemistry this appears not to be the case. To the layman's eye the clauses relating to the admission of Fellows simply exhibit the orthodox want of clearness and precision befitting a legal document when perused by a being of only ordinary intelligence; but to the legal vision they imply much more—no less, indeed, than the absolute prohibition from doing the very thing for which the Charter was most wanted! Such, at least, appears to be the result of "Counsel's opinion" upon the question as to whether an examination can or cannot be imposed on candidates for Fellowship. In short, it seems that the Charter, the object of which was to enable the professional competence of Fellows to be ascertained and certificated, does not permit the Institute to accomplish the *raison d'être* of its existence!

The nett result of this somewhat startling discovery is that in the new scheme recently elaborated by the Council for improving the examinational system, it has been found impracticable to do anything whatever in the way of subjecting to a thorough sifting and testing process the professional qualifications for Fellowship possessed by candidates for that rank; so that in future, as heretofore, the possession of the Fellowship will be in no way a guarantee of sound professional training in some particular given direction, but will only imply that a decent sort of preliminary scientific education has been obtained.

It becomes, therefore, a matter for serious consideration as to whether steps should not be speedily taken with the object of resigning the present Charter and obtaining instead a new one wherein the powers prayed for are actually given without the possibility of mistake or misconstruction.

In a short time the Annual Meeting of Members will take place, when it might be well that this question should be discussed. As the writer's term of office on the Council will then expire, it will be out of his power to put forward his views in the ensuing year before the then reigning Council; wherefore the present communication.—I am, &c.,

C. R. ALDER WRIGHT.

THE VOLATILE FATTY ACIDS OF BUTTER.

To the Editor of the Chemical News.

SIR,—I must ask you to allow me space in your next issue to reply to Mr. H. Droop Richmond's "Note" in

the CHEMICAL NEWS, vol. lxxi., p. 235, known, in legal phraseology, as constructive libel.

I am obliged to my critic for calling my attention to the error; it is a clerical one, one of transition when calculating the percentage, not an arithmetical one, such as that made by Mr. H. Droop Richmond in his readable English; and, before he becomes an authority on simple arithmetic, it is to be hoped he will study the subject more closely, for by so doing "There is hope, then, that in a few years he may find the same results as other observers."

I refrain for the present from commenting further upon his communication, but I think it would be advisable if Mr. Richmond would unreservedly withdraw his insinuations, as I candidly admit that with this particular sample I cannot go beyond the guarantee of the Aylesbury Dairy Co., from whom I received the butter, and I have every reason to believe it was the best English butter.—I am, &c.,

WILLIAM JOHNSTONE.

13, Fish Street Hill, London.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 20, November 14, 1892.

Combustion-Heat of Camphor.—M. Berthelot.—M. Louguine found for the different isomeric states of camphor the following combustion-heats:—Dextrorotatory, 1404.2 cal.; levorotatory, 1416.0 cal.; inactive, 1415.4 cal. M. Stohmann, on the contrary, obtained for dextrorotatory camphor 1414.3 cal., and requested M. Berthelot to verify the result. Three determinations were accordingly made by different experimentalists. M. Matignon obtained +1414.2 cal.; M. Tassilly +1413.5 cal.; M. Aladern (mean) +1413.3 cal.

Observations on A. Colson's Paper on the Rotatory Power of the Salts of Diamine.—C. Friedel.—The plane which M. Colson takes as the plane of symmetry is not even a plane of symmetry in inactive tartaric acid, but perpendicular to the only plane of symmetry existing in the molecule constructed with representative tetrahedra.

Researches on the Chemical Constitution of Peptones.—P. Schutzenberger.—(1) The products precipitable by phosphotungstic acid present between the oxygen and the nitrogen a ratio approaching 1.27:1, and between the carbon and the hydrogen a ratio close upon 1:1.9. Under the action of baryta they lose nearly a fourth of their nitrogen as ammonia ($\frac{1}{3.66}$), a corresponding quantity of carbon dioxide (CO_2 for 2NH_3). The fixed and amidic residue from this treatment with baryta is of the form $p(\text{C}_n\text{H}_{2n}\text{N}_2\text{O}_4)$, or $\text{C}_m\text{H}_{2m}\text{NO}_2$, n being between 9 and 10 and bordering closely upon 9. (2) Products not precipitable by phosphotungstic acid present between oxygen and nitrogen a ratio near 2:1, and between carbon and hydrogen a proportion near 1:1.7. Under the influence of baryta they lose one-fifth of their total nitrogen in the form of ammonia, and a corresponding quantity of carbonic acid (CO_2 for 2NH_3), as also acetic acid (about 1 mol. for 2 mols. ammonia). The fixed and amidic residue of this treatment is of the form $p(\text{C}_n\text{H}_{2n}\text{N}_2\text{O}_6)$, or $\text{C}_m\text{H}_{2m}\text{NO}_3$. n comprised between 9 and 10 and very close upon 9. The portion soluble in alcohol gives analogous results, with the difference that there is an excess of hydrogen, the proportion C_nH_{2n} becoming close upon $\text{C}_n\text{H}_{2n}+2$.

Influence of the 'Distribution' of Manures in the Soil upon their Utilisation.—H. Schloesing.—The author gives the results of his experiments in the form of tables.

Study on the Pathogenic Power of Beetroot Pulp which has been Ensilaged.—M. Arloing.—The alimentary use of the pulp of beetroot preserved in silos produces various diseases in ruminants, sometimes with a fatal termination. The fatal dose of the juice drained from the pulp varies from 3 to 4 c.c. per kilo. of the living weight of the animal experimented upon. The liquid is most dangerous if the pulp has been kept in a silo for two months. The microbia suspended in the liquor play a less important part in the poisoning cases than the liquid itself. The poison resides in substances of microbian origin dissolved in the liquid. The author divides these substances into diastasic and ptomainic. The latter are convulsing and paralyzing, whilst the former exert a more persistent influence of the vaso-motive phenomena.

Attempt at a General Method of Chemical Synthesis.—Raoul Pictet.—(See p. 273).

Fusion of Calcium Carbonate.—H. Le Chatelier.—The author finds that the melting-point of calcium carbonate is a little below that of gold, which confirms the accuracy of the determination of Hall towards the end of the last century.

The Molecular Weights of Sodammonium and Potassammonium.—A. Joannis.—The ammoniums studied may be represented by the formulæ N_2H_6Na and $N_2H_6K_2$.

A Propylamidophenol derived from Camphor.—P. Cazeneuve.—The author by successive transformations has succeeded in producing a propylamidophenol not yet described by setting off from camphor. The result confirms the presence in this substance of the propyl or isopropyl group.

The Colouring-Matter of Pollen.—G. Bertrand and G. Poirault.—Carotine, $C_{40}H_{38}$, is the colouring-matter of the yellow or orange pollens. It has probably a different physiological function in leaves and on the surface of pollen.

The Rotatory Power of Solutions.—M. Wyrnoff.—The author concludes that the rotatory power of dissolved substances, like the rotatory power of crystalline bodies, is a phenomenon of a reticular order, which depends on the symmetry peculiar to the crystalline net. The particle which exists in solution retains this symmetry, and as this symmetry depends not alone on the chemical molecule, but also on the water of crystallisation (or whatever replaces it), there is no dissociation in the solution, nor, still less, separation into the electrolytic elements which are designated as ions.

On Vital and Chemical Fermentations.—Maurice Arthur and Adolphe Henri.—Sodium fluoride in the proportion of 1 per cent arrests instantly and finally vital fermentations without suspending the chemical fermentations. It thus enables us to distinguish the phenomena of these two groups.

MEETINGS FOR THE WEEK.

MONDAY, Dec. 5th.—Society of Arts, 8. (Cantor Lectures). "The Generation of Light from Coal-Gas," by Prof. Vivian B. Lewes.

Medical, 8.30.

Society of Chemical Industry, 8. (1) "A New Form of Filter Press for Laboratory Use," by C. C. Hutchinson. (2) "The Production of Acetic Acid from the Carbohydrates," by Messrs. Cross and Bevan. (3) "Electrolytic Soda and Chlorine: The Present Aspects of the Question," by Messrs. Cross and Bevan.

TUESDAY, 6th.—Institute of Civil Engineers, 8. Pathological, 8.30.

WEDNESDAY, 7th.—Society of Arts, 8. "The Chicago Exhibition, 1893," by James Dredge, Geological, 8.

THURSDAY, 8th.—Royal, 4.30.

Royal Society Club, 6.30.

Mathematical, 8.

Institute of Electrical Engineers, 8. (Anniversary).

FRIDAY, 9th.—Physical Society, 5. "On Colour Vision," by W. B. Croft. "On Magic Mirrors," by Professor S. P. Thompson. "On Reflection from Diffusing Surfaces," by Dr. Sumpster.

Astronomical, 8.

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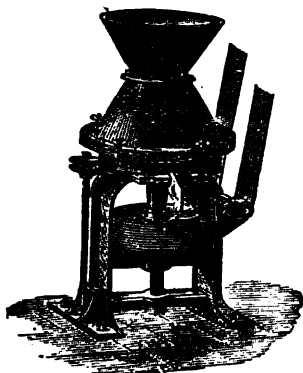
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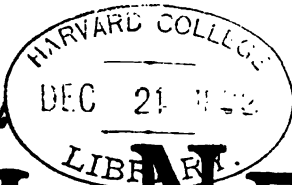
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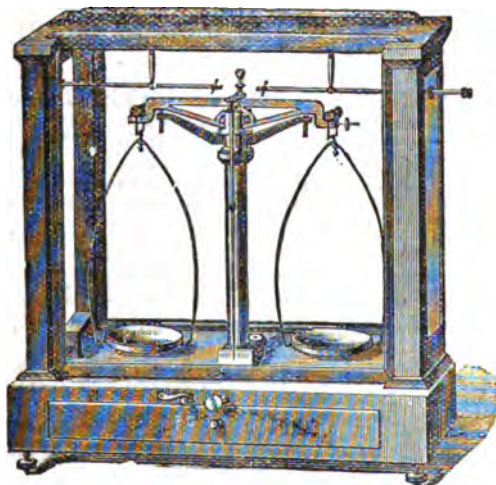


FIG. 3A.

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THE CHEMICAL NEWS.

VOL. LXVI., No. 1724.

ON THE PRESENCE OF MAGNETITE IN CERTAIN MINERALS AND ROCKS.*

By A. LIVERSIDGE, M.A., F.E.S.,
Professor of Chemistry in the University of Sydney.

THE following experiments to determine the amount of magnetite or of magnetic particles in minerals and certain rocks were made in consequence of the following statement in Bauerman's "Systematic Mineralogy," p. 298, 1881, viz.:—"Chrome iron and Franklinite are magnetic, but it is not certainly known whether this is a special property or caused by finely interspersed magnetite." Other writers, like Dana, simply state that the above minerals are magnetic, but do not make any comment as to whether the magnetic properties are inherent in the minerals named or due to enclosed magnetite; hence I thought it would not be altogether a waste of time to put the matter to the test of experiment. Accordingly I had some of the more common ferruginous and magnetic minerals crushed to a fine powder, sifted through a No. 60 sieve, and then acted upon by an electro-magnet under water. An electro-magnet was used because it is very difficult to brush off all the magnetic particles from an ordinary permanent bar or horse-shoe magnet, even when the armature is on. The magnet used lifted a weight of 18 ounces. A comparatively feeble one was purposely used, so as to attract and remove only those particles which would be attracted by a good ordinary permanent magnet; a powerful electro-magnet would not have been so suitable for the object in view.

The crushing was effected in a porcelain mortar, and finished in an agate one, to prevent access of particles of iron, which of course are always abraded from iron pestles and mortars. The non-magnetic matter can only be separated from the magnetic portions by repeated applications of the magnet and re-grinding, because a certain amount of the non-magnetic powder is apt to be entangled with the magnetic.

Inasmuch as hæmatite, Fe_2O_3 , is often somewhat magnetic, this was chosen as one of the first minerals to be tested for magnetite.

1. *Hæmatite*.—A dark compact red hæmatite; locality unknown, but probably from Elba. Acted on magnetic needle. The powder yielded—

	Grms.
Magnetic particles	10.15
Non-magnetic	56.80

66.95

Or 15 per cent of magnetite.

2. *Hæmatite*.—Dark red botryoidal massive hæmatite, mixed with a little quartz. Frizenton, Cumberland, England. Yielded no magnetic particles.
3. *Hæmatite*.—The same as the last, but a softer variety. This also did not yield any magnetic particles.
4. *Micaceous Hæmatite*.—From the island of Tanna, where it is used by the natives for dusting over the body, for ornamental purposes, on account of its being in the form of bright glistening scales. This specimen is evidently of recent volcanic origin, and resembles the micaceous iron ore from Vesuvius and other volcanoes. It did not yield any magnetic particles.

5. *Micaceous Hæmatite*.—Locality unknown. Yielded traces of magnetic particles.

	Grms.
Weight of powder	18.7
Weight of magnetic particles ..	0.122
Percentage of magnetic particles	0.6

6. *Brown Hæmatite*.—Hydrated sesquioxide of iron. A hollow concretion; locality unknown, but probably from the Waianamatta shale: of a dark reddish brown colour. 51 grms. were crushed, but no magnetic particles obtained.
- 6A. *Stalactite* of hydrated sesquioxide of iron from Berrima, N.S.W. 26.62 grms. yielded only a trace of magnetic oxide.
7. *Dark Brown Hæmatite*.—Locality unknown. 22.5 grms. were treated, but no magnetic particles obtained.
8. *Brown Hæmatite*.—Compact and of a dark yellowish brown colour, from Kandern, Baden. 44 grms. were treated, but no magnetic particles were obtained.
9. *Goethite*.—Yellow fibrous structure; from Kleinschmalkalden, Hessen. No magnetic particles were obtained from 43 grms.
10. *Goethite*.—Crystallised; from Lostwithiel, Cornwall, England. No magnetic particles.
11. *Goethite*, from Wallerawang, from irregular deposits in the sandstone. Yielded an almost black powder. No magnetic particles.
12. *Brown Hæmatite* from the quarry above the House of Correction, Hobart, Tasmania, where it occurs in thin crystalline plates, filling joints in the rock, which are about $\frac{1}{4}$ inch across. Free from magnetic particles.
13. *Brown Iron Ore*.—From Hungary. Compact dark yellow coloured. No magnetic particles from 58 grms. of the powder.
14. *Stalactitic Brown Hæmatite*.—Wallerawang, N.S.W., with bright black psilomelane-like coating. No magnetic particles.

Analysis.

Moisture	1.28
Combined water	12.04
Iron sesquioxide	73.60
Phosphoric oxide	0.12
Sulphur trioxide	0.06
Insoluble in acid	12.19
Loss	0.71

100.00

[See "Minerals of New South Wales," p. 96.]

15. *Brown Hæmatite*.—Dark brown in colour. No magnetic particles from 33 grms. of the powder.
16. *Brown Hæmatite*.—Wallerawang. Massive. Gave dark red-brown powder. May have been "roasted" in a bush fire. No magnetic particles.
17. *Brown Hæmatite*.—Wallerawang. Loose structure. Gave yellow-brown powder. No magnetic particles.
18. *Loose Brown Hæmatite*.—Wallerawang. No magnetic particles.
19. *Brown Hæmatite*.—Near Hobart, Tasmania. Dark brown colour; massive. Yielded light brown powder. No magnetic particles.
20. *Pea Iron Ore*.—Brown hæmatite. Locality unknown. No magnetic particles.
21. *Brown Hæmatite*.—New Guinea. Yielded a trace of magnetic particles.
22. "*Ironstone*."—Brown hæmatite. Reigate, Surrey, England. No magnetic particles.
23. *Limonite*.—Clay Band, Wallerawang, N.S.W.: of a dark red-brown colour, looks as if it had been calcined; powder also red. A trace only of magnetic particles.

* From the Transactions of the Australasian Association for the Advancement of Science, Hobart Meeting, 1892.

24. *Limonite*.—Clay Band, Wallerawang, N.S.W. No magnetic particles.
25. *Brown Hematite*.—Brazil. Pseudomorphous after iron pyrites, auriferous. No magnetic particles.
26. *Ferrous Carbonate*.—Jamberoo, N.S.W. See "Minerals of New South Wales," p. 99. 35.1 grms. of powder yielded no magnetic particles. In another case 64 grms. of powder were also found to be free from magnetic particles.
27. *Iron Carbonate*.—A nodule from the coal measures, England. No magnetic particles.
28. *Iron Carbonate*.—A septarian nodule. No magnetic particles.
29. *Kraussite or Dufrenite*.—Green iron ore, hydrated iron phosphate. Ullersreuth, near Hof. No magnetic particles.
30. *Hornblende Schist*.—New Caledonia. Contained a little magnetite.
31. *Spinel* (Magnesium aluminate).—Ceylon. Red, transparent. No magnetic particles.
32. *Spinel*.—Elba. No magnetic particles.
33. *Spinel*.—Warwick, New York, U.S.A.; in large black octahedra. 32.102 grms. yielded 0.094 grm. of magnetite. Spinel crystallises in the same form as magnetite, and has the same general formula; hence the presence of magnetite, even in quantity, would not be surprising.
34. *Garnet*.—Franklin, New Jersey, U.S.A. Common iron alumina garnet of a brown-red colour. Did not yield any magnetic particles.
35. *Franklinite*.—Sussex Co., New Jersey, U.S.A. Strongly magnetic; 28.292 grms. yielded 9.131 grms. of magnetic particles, or 32.23 per cent.
36. *Chrome Iron*.—New Caledonia. Massive, black, with granular structure, but mixed with some steatite. When crushed the powder was of a grey tint, and did not yield any magnetic particles.
37. *Chrome Iron*.—New Caledonia. Massive, black. 95.7 grms. yielded 0.663 grm., or 0.69 per cent of magnetic particles.
38. *Chrome Iron*.—Wollomi, N.S.W. Black, massive; no visible foreign matter except a few particles of steatite. 100 grms. of powder only yielded a trace of magnetite.
39. *Pyrrhotine*, or magnetic pyrites, was found to be wholly attracted by the magnet, *i.e.*, its magnetic properties are apparently not due to the diffusion of particles of magnetite throughout its substance.
- 39A. *Pyrrhotine*, from Sala, Sweden, was also found to be wholly magnetic, except a small quantity of associated earthy gangue.
40. *Auriferous Hematite*.—Mount Morgan. 11.53 grms. were crushed and passed through a 60 sieve. No magnetite found.
41. *Jeweller's Rouge*.—Found to be free from magnetic particles.
42. Artificially prepared dry ferric hydrate was also found to be free from magnetic particles.
43. *Bornite*, or Purple Copper Ore.—Carn Brae Mine, Cornwall, England. Did not yield any magnetic particles.
44. *Iron Pyrites*.—Joshua's Creek, Taupo, New Zealand. The specimen is of recent origin, and in process of deposition round decaying wood and twigs in the stream of hot water supplying the baths. In parts it is black and powdery, but was found to be free from magnetic particles.
45. *Tinstone Conglomerate*.—Vegetable Creek, New England, N.S.W. This consists of rolled tinstone, quartz, &c., cemented together by iron oxide. 62.4 grms. of the powder was sent through a 60 sieve, but no magnetic particles were detected.
46. *Serpentine*.—Dark oily green colour, from Tasmania. 234 grms. yielded 8.4 grms. magnetic particles. Magnetic portion = 3.589 per cent. Another specimen of 50 grms. yielded 2.389 grms. of magnetite.
47. *Serpentine*.—Tasmania. Green, with visible specks of magnetite. 356.5 grms. gave 28.501 grms. of magnetic particles, or 7.99 per cent.
48. *Serpentine*.—New Caledonia. Dark brown, with veins of steatite and of magnetite. 212 grms. gave 5.92 grms. of magnetic particles, or 2.79 per cent.
49. *Serpentine*.—New Caledonia. Similar to last. 173.5 grms. gave 8.86 grms. of magnetic particles, or 5.10 per cent.
50. *Serpentine*.—New Caledonia. 26.2 grms. gave a trace only of magnetic particles.
51. *Serpentine*.—New Caledonia. 62.20 grms. gave 1.990 grms. of magnetic particles, or 3.19 per cent.
52. *Serpentine*.—New Caledonia. 25.7 grms. gave 3.67 grms. of magnetic particles, or 14.28 per cent.
53. *Serpentine and Asbestos*.—Tasmania. 24.0 grms. gave only a trace of magnetite. All the asbestos was separated before crushing.
54. *Serpentine*.—Lucknow, N.S.W. Very dark, almost black, with thin films of steatite. 33.80 grms. gave 7.773 grms. magnetic particles, or 22.99 per cent. A second specimen of the same, weighing 24.149 grms. yielded 6.08 grms. magnetite, or 25.13 per cent.
55. *Serpentine*.—Scotland. 28 grms. gave no magnetic particles.

All the serpentines examined acted upon a common five-inch magnetic needle, except Nos. 50, 53, and 55; No. 47 from Tasmania, and 49 from New Caledonia, were also distinctly polar. No nickel iron or awaruite was found in any of the serpentines.

Conclusion.

As far as the foregoing experiments are concerned, they show that in the specimens examined the magnetic properties of chrome iron, franklinite, spinel, garnet, some hematites, and other minerals and rocks are due to the presence of scattered particles of magnetite. In most cases the magnetic separated portion was further tested chemically, and proved to be magnetite, but it was not thought necessary to do this in every case. The pyrrhotine, however, appears to possess inherent magnetic properties.

THE QUANTITATIVE DETERMINATION OF RUBIDIUM BY THE SPECTROSCOPE.*

By F. A. GOOCH and J. I. PHINNEY.

(Concluded from p. 265).

It appears that within limits the presence of sodium in the flame increases the brilliance of the rubidium spectrum. The brightness of the lines is raised under the conditions to a maximum by the presence of sodium to 40 per cent of the weight of the rubidium, and increase in the amount of sodium does not further influence the brightness of the lines until the proportion of sodium to rubidium is as ten to one; or, speaking broadly, the difference between the dissociating effect of sodium upon the rubidium chloride (to which we attribute the effect noted) does not appear to be materially different whether one or a score of molecules of sodium chloride are present to one of the rubidium chloride. But when the proportion of sodium to rubidium much exceeds ten to one the glare of light diffused through the entire spectrum (though

Standard. Rubidium in a coil-full (1-50 c.m.)	Test solution. Rubidium in a coil-full with eighth-tenths of its weight of sodium.	Line of test compared with standard.
0.00066 m.grm.	0.00066 m.grm.	Brighter.
" "	0.00048 "	"
" "	0.00046 "	"
" "	0.00044 "	Equally bright.

* From the *American Journal of Science*, vol. xlv., Nov., 1892.

the sodium line itself may be cut off) begins to affect the vision, and as the increase advances ultimately extinguishes the rubidium lines utterly. The degree of increase in brilliance when the lines are at a maximum was determined by diluting the test-solution until a coil-full gave a line equally brilliant with that of the standard.

It is plain that at the maximum degree of brilliance the sodium is responsible for an increase of 50 per cent in the brightness of the lines.

The details of similar experiments in which potassium chloride was introduced into the flame with the pure rubidium chloride are given in the accompanying tabular statement.

Standard. Rubidium in a coil-full (1-50th c.m.). M.grm.	Test solution. Potassium in a coil-full. M.grm.	Comparison of lines of test taken by pairs.	Comparison of lines of test with standard.
0.00066	0.00020	Slightly fainter.	Brighter.
	0.00040	Slightly brighter.	
	0.00020	Fainter.	
"	0.00340	Brighter.	Brighter.
	0.00040		
"	0.00066	Equally bright.	Brighter.
	0.00040		
"	0.00340	Brighter.	Brighter.
	Fainter.		
0.00066	0.00066	Equally bright.	Brighter.
	0.00132		
"	0.00066	Brighter.	Brighter.
	Fainter.		
"	0.00340	Brighter.	Brighter.
	Fainter.		
"	0.00066	Brighter.	Brighter.
	Fainter.		
"	0.00066	Brighter.	Brighter.
	0.01320	Fainter.	
"	0.00066	Brighter.	Brighter.
	0.02000	Fainter.	
"	0.00066	Brighter.	Brighter.
	0.02660	Fainter.	
"	0.00066	Brighter.	Brighter.
	0.03340	Fainter.	
"	0.00066	Brighter.	Brighter.
	0.03340	Invisible.	

From these results it appears that the presence of potassium produces an effect upon the rubidium lines similar to that of sodium; and, furthermore, the addition of 0.0004 m.grm. of potassium in the form of chloride to 0.00066 m.grm. of rubidium also in the form of chloride brings out the maximum brightness which is not materially changed by further addition of potassium up to about 0.0013 m.grm., but that the increase of the potassium to 0.0034 m.grm. results in diminution of brightness. In other words, it seems that a single molecule of potassium chloride has approximately the same dissociating effect upon the molecule of rubidium chloride in the flame as that brought about by a greater number, that the presence of potassium in the proportion of five parts to one of the rubidium begins to influence visibility unfavourably, that when this proportion rises to thirty to one of the elements (or twenty to one of the chlorides) the lines appear about as distinctly as if no potassium were present, and that an increase of proportion to fifty to one may bring about a sufficient glare of light to reduce the rubidium lines to invisibility. The degree of increase in brilliance due to the action of potassium when that element is present in proportions suitable to induce the maximum effect is shown in the following record.

Standard. Rubidium in a coil-full (1-50th c.m.). M.grm.	Test solution. Rubidium in a coil-full with its own weight of potassium. M.grm.	Line of test compared with standard.
0.00066	0.00066	Brighter.
"	0.00064	Brighter.
"	0.00057	Brighter.
"	0.00049	Brighter.
"	0.00044	Equally bright.
"	0.00040	Fainter.

It appears that the presence of 0.00044 m.grm. of potassium is capable of increasing the brilliance of the lines yielded by 0.00044 m.grm. of rubidium to an equality with the lines given by 0.00066 m.grm. of the pure salt; or, that the maximum increase of brightness amounts to 50 per cent.

It is evident, therefore, that means must be found to effect the separation of the rubidium from sodium and potassium, or of bringing test and standard to the same condition as regards the presence of these elements, before any reasonable degree of accuracy can be expected in the spectroscopic determination of rubidium as it ordinarily occurs in nature. The separation from sodium is easily accomplished by the conversion of the salts to the form of chloroplatinates; but for the quantitative separation of rubidium from potassium there is no good method known. The question as to the practical value of the spectroscopic reaction of rubidium for purposes of approximate quantitative analysis resolves itself into the problem as to whether by matching potassium lines as well as rubidium lines (following the method outlined in the determination of potassium in presence of sodium), and so bring the lines of test and standard equally under the influence of potassium, it is possible to make the comparison between the rubidium lines trustworthy. It was shown in the former paper that in matching solutions of potassium by means of the red line there is no difficulty; but the convenience of being able to use the spectroscope without re-adjustment throughout the entire experiment made it desirable to see whether the blue line of potassium might not serve sufficiently well in the comparison. It is hardly necessary to reproduce here in detail the evidence bearing upon this point, but we found as the result that the potassium may be determined by the use of the blue line with an error amounting to 10 per cent or 20 per cent, which, though far greater than that inherent in the use of the red line, admits of the attainment of determinations which should be accurate enough for the present purpose. We proceeded, therefore, to make a determination of rubidium in presence of potassium by the process referred to, the details of which are given in Experiment IV.

Experiment IV.

Standard solution containing { 0.0005 m.grm. rubidium }
 { 0.0015 " potassium }

to the coil-full.

Test solution contained 8 m.grms. rubidium and no potassium.

STEP 1.—*Preliminary Test for Rb.*—Test at 20 c.m.* gave Rb line like standard.

STEP 2.—*Preliminary Matching of K Line.*—Test at 20 c.m.* gave K line like standard when 1 m.grm. of K had been added.

STEP 3.—*Re-matching of Rb Line.*—Test at 35 c.m.* gave Rb lines like standard.

STEP 4.—*Re-adjustment of K Line.*—Test at 35 c.m.* gave K line like standard when 2 m.grm. were present.

STEP 5.—*Final Matching of Rb Line.*—Test at 35 c.m.* gave Rb line like standard.

	M. grm.
Rubidium found 35×50×0.0005	=0.875
" taken	=0.8
Error	=0.075 =9.4 per cent.

It is evident that the percentage error is considerable, but inasmuch as the application of the process would naturally be to the determination of small absolute amounts of rubidium, we thought it desirable to go a step further to see whether means are at hand for separating large amounts of potassium from small amounts of rubidium with an approach sufficiently near to completeness to bring the potassium present within the limits allowed by the spectroscopic method. After some experiments

tion we fixed upon the simplest possible procedure, viz., the solution of the salts in the least possible amount of water, precipitation of the mass of potassium chloride by addition of alcohol, filtration, and the evaporation of the filtrate. In Experiments V., VI., VII., this mode of working was put to the proof. The amounts of rubidium indicated were dissolved in the form of the chloride in water, 0.1 grm. of potassium chloride was added, and the solution was evaporated and treated as described.

	Rubidium taken in the form of chloride. M.grms.	Potassium taken in the form of chloride. Grm.	Rubidium found. M.grms.	Absolute error. M.grm.	Percentage error. Per cent.
V.	1	0.1	0.8	0.2	20
VI.	2	0.1	1.7	0.3	15
VII.	1	0.1	0.9	0.1	10

The error of the process is manifestly large, and only roughly approximate results can be hoped for when large amounts of rubidium are dealt with; but, if the question is the estimation of only a few m.grms. of rubidium, it will appear, we think, in view of the fact that the only alternative is an indirect process, that even this great error is not absolutely prohibitive of what may be called fair determinations.

STANDARD IODINE SOLUTION:

A METHOD FOR ITS PREPARATION.

By H. L. PAYNE.

OF the methods proposed for determining sulphur in iron and steel, that first suggested by Elliott (*CHEMICAL NEWS*, xxiii., 61) merits attention on account of the ease and celerity of manipulation, as well as accuracy of the results obtained. This last point has been held in question by many chemists, but the record obtained by Lee S. Clymer, of the Crane Iron Co. (see *Journ. Anal. Appl. Chem.*, June, 1892) places it on a par with those longer methods which have been considered highly accurate.

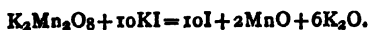
The essential feature of Elliott's method is the titration of the sulphur evolved as hydrogen sulphide, with a standard solution of iodine. Several methods are in use for the preparation of this solution of iodine.

The one given in Blair is tedious, in that it involves the use of two other standard solutions, one of potassium bichromate, and another of sodium thiosulphate, as well as an indicator solution of starch; moreover, the use of ammonium carbonate to retard the decomposition of the thiosulphate introduces a serious error in the titration, as has been pointed out by Topf (*Zeit. Anal. Chem.*, 1887, p. 137).

Mohr's method by weighing clear crystals of thiosulphate, and Fresenius's method by re-subliming and weighing the iodine direct, are both shorter and better.

A solution may also be made sufficiently exact for most uses by weighing 4 grms. iodine to the litre where 5 grms. of iron are taken for analysis, but like all the above methods it involves an uncertain error.

We have used for some time the following method and find it eminently satisfactory in every way. It depends upon the reaction between potassium permanganate and potassium iodide in solution:—



Sufficient acid, preferably sulphuric, is added to keep the manganese in solution and to render the fluid slightly acid. This reaction takes place in the cold and proceeds to completion even in dilute solutions. The strength of the permanganate solution being known, we can readily determine the amount of iodine liberated. One equivalent of potassium permanganate liberates 10 atoms of iodine, or oxidises ten atoms of iron. Hence, one atom of iron corresponds to one atom of iodine, and as one

atom of sulphur reacts with two atoms of iodine, two atoms of iron equal one atom of sulphur; or 128 grms. iron are equivalent to 32 grms. sulphur. Therefore the sulphur value of our permanganate solution will be $\frac{1}{11}$, or one-fourth of its iron value.

In preparing a standard iodine solution by this method, we are accustomed to proceed as follows:—

Take about 10 grms. potassium iodide in a litre flask; add 10 to 15 c.c. dilute sulphuric acid, and run in the calculated amount of potassium permanganate solution from a burette. Agitate a few moments until the reaction is complete and the solution clears, and dilute to the mark with water. A litre of such a solution can be prepared inside of two minutes in any laboratory having a standard permanganate solution constantly on hand, and there is, therefore, no necessity for keeping a standard iodine solution long enough to have it change materially.

A solution of permanganate such as is used in Emmerton's method for phosphorus titrates 6.141 grms. iron per litre, and of such a solution 32.7 c.c. will make one litre of iodine solution titrating 0.01 per cent sulphur per c.c. on 5 grms. iron or steel taken.

As an absorbent for the hydrogen sulphide, common white potash is to be preferred; potash purified by alcohol should be avoided. Dilute sulphuric acid may be used with advantage in acidifying the potash solution. The addition of methyl-orange to the starch solution in sufficient quantity to give a perceptible red colour to the solution to be titrated will, by turning colourless or a faint yellow on acidifying, indicate when an excess of acid has been added.—*Journal of Analytical and Applied Chemistry*, vi., No. 9.

THE ELECTROLYSIS OF METALLIC FORMATES.*

By HILL SLOANE WARWICK.

(Continued from p. 275).

ELECTROLYTIC SEPARATIONS.

Cadmium from Manganese.

	Cadmium taken. Grm.	Manganese taken. Grm.	Cadmium found. Grm.	Free acid. C.c.	H ₂ O. C.c.	OH gas per min. C.c.	Time Hrs.	Diff. from theory. Percent.
1.	0.0497	0.0554	0.0425	35	75	0.8	16	—
2.	0.0497	0.0554	0.0440	35	75	1	16	—
3.	0.0497	0.0554	0.0498	25	75	2.7	17	+0.20
4.	0.0511	0.0554	0.0509	20	75	2.4	19	-0.39
5.	0.0511	0.0554	0.0697	5	150	2.7	18	—
6.	0.1022	0.1108	0.1098	20	75	2.5	17	—
7.	0.1022	0.1108	—	40	150	2.8	45	—
8.	0.0511	0.0554	0.0514	30	75	2.7	18	+0.58

In the preliminary experiments on manganese alone it was found that the presence of 20 c.c. of free acid was sufficient to prevent the deposition of any peroxide on the cathode, except in the very slightest traces; but the presence of cadmium in the solution, seemingly, had a contrary effect, as the presence of even 40 c.c. of acid failed to prevent the separation of traces of manganese on the negative pole 7. In 5, to which 5 c.c. of free acid had been added, the deposit of peroxide of manganese upon the negative pole was almost five times greater than in a solution of manganese to which no cadmium had been added, all the other conditions being the same. In all the above experiments the platinum dish was used as the anode, the platinum crucible serving as the negative electrode. In 1 and 2 the cadmium was not completely

* Read before the American Philosophical Society, November 6, 1891. From the *Proceedings of the American Philosophical Society*, xlix., No. 136.

deposited. Traces of cadmium were found in 6 and 7. More or less manganese was found in all the deposits, but only in traces in the presence of more than 20 c.c. of free acid; 4 and 7 were very spongy; the others were slightly so at the periphery of the crucible, but adherent. The best results were obtained by fulfilling the conditions described in 3, 4, and 8; but to obtain a compact deposit of cadmium free from all traces of manganese, it is evident that the amount of free acid must be increased and the poles separated. Under these conditions a stronger current must be employed than that furnished by the battery of "crowfoot" cells, with which my experiments were carried on.

Zinc from Manganese.

Zinc taken. Grm.	Manganese taken. Grm.	Zinc found. Grm.	Free acid. C.c.	H ₂ O. C.c.	OH gas per min. C.c.	Time. Hrs.	Diff. from theory. Perct.
1. 0.0562	0.0554	—	30	90	2.9	17	—
2. 0.0562	0.0554	—	20	100	2.9	16	—

The dish served as anode, the crucible as cathode. Both were failures, the zinc being spongy and containing MnO₂, and not entirely precipitated.

Copper from Zinc.

Copper taken. Grm.	Zinc taken. Grm.	Copper found. Grm.	Free acid. C.c.	H O. C.c.	OH gas per min. C.c.	Time. Hrs.	Diff. from theory. Perct.
1. 0.1074	0.0818	—	5	100	1.8	46	—
2. 0.1074	0.0818	—	5	100	1.2	17	—
3. 0.1074	0.1124	—	5	100	0.8	16	—
4. 0.1074	0.0818	0.1072	15	100	0.8	16	-0.18
5. 0.1074	0.0818	0.1073	20	100	0.8	17	-0.09
6. 0.0987	0.0818	0.0990	20	100	0.8	17	+0.30
7. 0.0987	0.0818	0.0984	20	100	0.6	16	-0.30
8. 0.1057	0.1006	0.1052	15	100	0.8	16	-0.47
9. 0.1057	0.1006	0.1061	15	100	0.8	18	+0.37
10. 0.1057	0.1006	0.1058	15	150	0.8	18	+0.09
11. 0.1057	0.1006	0.1059	20	150	0.8	19	+0.18
12. 0.1057	0.1006	0.1053	20	150	0.8	21	-0.37
13. 0.1057	0.1006	0.1060	20	150	0.8	16	+0.28

As will be seen from the above it was possible to separate copper free from zinc, except the slightest traces, by using a weak current in solutions to which 15—20 c.c. of free formic acid had been added. By employing stronger currents, or diminishing the amount of free acid, the copper was deposited admixed with considerable quantities of zinc. If the necessary precautions are observed no zinc will be deposited, and the copper will be compact and adherent.

Cadmium from Zinc.

Cadmium taken. Grm.	Zinc taken. Grm.	Cadmium found. Grm.	Free acid. C.c.	H ₂ O. C.c.	OH gas per min. C.c.	Time. Hrs.	Diff. from theory. Perct.
1. 0.1231	0.0818	—	15	100	0.2	17	—
2. 0.1231	0.0818	0.1229	30	100	0.8	19	-0.16
3. 0.1231	0.0818	0.1234	30	100	0.8	43	+0.24
4. 0.1231	0.0818	0.1426	35	100	1.25	16	+15.83
5. 0.1231	0.0818	0.1233	30	100	0.8	16	+0.16
6. 0.0492	0.0409	—	15	100	0.8	16	—
7. 0.0492	0.0409	0.0842	15	100	1.25	16	—
8. 0.0984	0.1026	0.0322	35	100	0.8	19	—
9. 0.0492	0.0409	0.0494	15	100	0.8	41	+0.40
10. 0.0984	0.1026	0.1735	35	100	1.25	17	—
11. 0.0984	0.1026	0.0722	35	75	0.8	17	—
12. 0.0984	0.1026	0.0982	25	125	0.8	18	-0.20
13. 0.0984	0.1026	0.0985	25	125	0.8	16	+0.10
14. 0.1004	0.1006	0.1001	25	125	1	48	-0.29
15. 0.1004	0.1006	0.0993	25	125	1	17	-1.09
16. 0.1004	0.1006	0.1000	25	125	1	17	-0.39
17. 0.1004	0.1006	0.1001	25	125	1	18	-0.29
18. 0.1004	0.1006	0.1008	25	125	1	20	+0.39
19. 0.1004	0.1006	0.0999	25	125	1	16	-0.49

The first seven determinations were made in a platinum dish weighing about 67 grms.; the remainder in a much larger dish weighing 117 grms. The results obtained with the latter were not as satisfactory as with the smaller dish (2, 3, 5), although a qualitative examination of the deposit and solution proved that the separation was complete (9, 12—19). The distance between the poles materially influences the results. In 6 the positive pole was in close contact with the dish; the cadmium contained zinc. In 9 the conditions were similar in all respects to the preceding, except that the distance between the poles was 2.5 c.m.; the deposit was free from zinc. With 0.2 c.c. OH gas per minute, only a small quantity of the cadmium was separated (1), the greater portion remaining in solution. With 1.25 c.c., on the other hand, the zinc was deposited as a dark grey coating upon the cadmium (7), even in the presence of 35 c.c. of free acid (10). In solutions containing 0.10 gm. of each metal a current of 0.8—1 c.c. HO gas per minute sufficed to secure a satisfactory deposit in the presence of 25 c.c. formic acid (12—19). With smaller quantities of metal (9) 15 c.c. of free acid was sufficient. The deposits in the above experiments were adherent and compact. There was no tendency to sponginess even in deposits containing large quantities of zinc.

(To be continued).

THE ARTIFICIAL PRODUCTION OF MINERAL SULPHIDES.

By H. N. WARREN, Research Analyst.

THE formation of sulphides by direct combination of the element sulphur with metallic substances usually affords little, if any, similitude to the natural or mineral form of the same compound. The reduction of sulphates by suitable means may be regarded as more imitative, but by employing as a reducing agent potassium sulphocyanide and bringing into contact with the same readily reducible oxides, the author has succeeded in imitating the natural sulphides to such a marked extent as to render detection impossible: or at other times producing in several cases entirely new compounds.

In the first instance, I will mention the action of KCNS upon litharge at a very low red heat; scaly litharge is almost immediately converted into galena, which, after washing, rivals in colour the native compound. The same substance, on raising the temperature to fusion under a layer of KCNS, breaks with an identical fracture, and possesses almost the same specific gravity as the dressed ore. Ferric oxide subjected thus to a continuous red heat yields brilliant pyrites, whilst at a still higher temperature the compound Fe₂S₃ is obtained, which may be also obtained by passing the vapour of CS₂ over metallic iron. Black oxide of manganese when treated with a large excess of KCNS and heated to bright redness, yields pyrolusite. Stannic oxide, as also the corresponding oxide of antimony, yields at high temperatures the ordinary sulphides; whilst at lower temperatures the golden sulphides have been obtained, possessing in all respects the full brilliancy of these compounds. Oxide of zinc treated thus yields a sulphide possessing very slight resemblance to the natural compounds, but, on the other hand, closely compares with the commercial pigment, though inferior as regards colour.

Phosphorescent sulphide of zinc has been already noticed on previous pages; it may therefore be of interest to state that several samples of zinc sulphide so prepared, after carefully cleansing the same from contaminated impurities, possessed this property in a marked degree.

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PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE following are abstracts of papers received during the vacation and published in the *Transactions* :—

44. "*Some Homonuclear Tri-derivatives of Naphthalene (Peridibromonaphthalene).*" By R. MELDOLA, F.R.S., and C. H. DESCH (*Trans.*, 1892, 765).

It is shown that Prager's statement (*Ber.*, 1885, 2163) that the NH_2 group in 2-nitro-4-bromo-1-amidonaphthalene cannot be displaced by bromine by Sandmeyer's method is incorrect; and a description is given of the 1:4-dibromo-2-nitronaphthalene, and also of the corresponding chlorobromo- and iodobromo-naphthalenes; all three substances are described as crystallising in small *ochreous* needles melting at 117° . On reduction, they yield amines almost destitute of basic properties, which readily oxidise in air; their acetyl derivatives crystallise in white needles, bromiodo- β -acetnaphthalid melting at 235° , the chloriodo-compound at 218° .

A lengthy footnote is appended to the paper, in which the conclusion arrived at by Armstrong and Rossiter (*Proc. Chem. Soc.*, No. 104, vii., 186), that when a mixture of ortho- and para-nitracetnaphthalid is brominated, the ortho-compound is alone attacked, is corroborated; and in which the interesting statement is made that one of the authors and F. W. Streatfeild have prepared peridibromonaphthalene from 1:1'-nitrobromonaphthalene: this new dibromonaphthalene melts at about 109° .

45. "*A Method of Measuring the Vapour Pressures of Solutions.*" By THOMAS EWAN, B.Sc., Ph.D., and W. R. ORMANDY (*Trans.*, 1892, 769).

A condensation hygrometer for determining vapour pressures of solutions at ordinary pressures is described and figured. The hygrometer consists of a thin polished silver cup soldered to a stronger ring of brass, which in its turn is cemented into a glass tube by means of tinfoil and sulphur; the upper end of the tube is closed with a cork through which pass a thermometer and an open tube carried down below the surface of the ether placed in the silver bulb, a side tube near the top being connected with an aspirator in such a way that the amount of air passing through the ether is under the control of the observer. The hygrometer is suspended in a glass vessel containing the solution under examination; this consists of a cylindrical bulb with a long narrow neck, a narrow side tube through which the rod of a stirrer passes being sealed into the shoulder of the bulb. The temperature is determined at which dew first becomes visible on the silver bulb.

Results obtained with solutions of sodium and cupric chloride are given in the paper.

46. "*The Hydrazines of Quinoline.*" By S. F. DUFTON, B.A., D.Sc. (*Trans.*, 1892, 782).

A description is given of an improved method of nitrating quinoline, and of a variety of derivatives prepared from the ana-compound.

To nitrate quinoline, the nitrate prepared from 50 grms. is added in about five portions to 50 c.c. of strong sulphuric acid contained in a litre flask, 10 c.c. of fuming sulphuric acid ($d=2.0$) being poured in after each introduction of nitrate, the mixture being kept cool. The yield is very good, 200 grms. of ana- and 150 grms. of ortho-nitroquinoline having been obtained from 300 grms. of quinoline in one operation. A small quantity (equal to about 3 per cent of the quinoline taken) of a dinitro-hydroxyquinoline is formed; this substance very closely resembles trinitrophenol.

The compounds described are the ana-amine and hydrazine, the semicarbazide, pyruvic hydrazone, acetone hydrazone, benzaldehydehydrazone, and anaquinoline-methylpyrazolone prepared from the hydrazine and anaquinindole- α -carboxylic acid.

It is pointed out that in the case of both ortho- and ana-derivatives, one remarkable feature common to both is the intense red colour of the mon-acid salts of the amine and hydrazine. The pyruvic hydrazone separates from an aqueous solution as a bright red crystalline precipitate differing from the corresponding ortho-compound by being soluble in water and by its vivid colour; this, however, changes to yellow on drying, with loss of water of crystallisation.

47. "*The Origin of Colour.* (IV.) *Note on the appearance of Colour in Quinoline Derivatives and of Fluorescence in Quinine Salts.*" By HENRY E. ARMSTRONG (*Trans.*, 1892, 789).

Attention is directed to the fact that it could scarcely have been predicted that the anaquinoline derivatives such as are described by Dr. Dufton would manifest colour, and it is argued that they are probably quinoid compounds: that the appearance of colour, in fact, is conditioned by the occurrence of an isodynamic change involving the passage from the "centric" structure of quinoline to the "ethenoid" structure of a quinone. Further, it is suggested that it may eventually prove to be possible to explain the fluorescence of certain salts of quinine by the application of a similar principle.

[*Correction and Addendum.*—It is stated in the foregoing note that "The ortho-derivatives described by Dr. Dufton, excepting the pyruvic hydrazone, apparently are colourless substances." This, as Dr. Dufton has pointed out to the writer, is not the case. The mistake—an entirely inexcusable one—appears to have been made owing to the absence from Dr. Dufton's paper describing the ortho-compounds of any reference to the colour of the acid salts of the amine and hydrazine; it is only incidentally, in the paper on the ana-derivatives, that he mentions that the intense red colour of the mon-acid salts of the amine and hydrazine is a remarkable feature common to both ortho- and ana-series; although an entry of this fact was originally made when my attention was first called to the work, in writing out the "note," the descriptions of the individual compounds were apparently alone consulted, and the incidental reference to the colour of the ortho-compound was consequently overlooked.

Although at present deprived of the forcible argument which the non-appearance of colour in the ortho-series would afford, I see no reason to abandon my contention that the coloured ana-compounds are of peculiar structure. Dr. Dufton's discoveries have, in fact, added greatly to the interest attaching to the study of quinoline derivatives, and it is necessary that the ortho-derivatives should be examined with special care. So many cases are now known in which substances long regarded as uniform definite compounds have proved to be composite that it is justifiable, in my opinion, to regard the ortho-derivatives with suspicion until their homogeneity has been placed beyond question.—H. E. A.]

48. "*Dicarboxyglutaconic Acid.*" By S. RUHEMANN, Ph.D., and R. S. MORRELL (*Trans.*, 1892, 791).

The action of phenylhydrazine on ethylic dicarboxyglutaconic acid and its benzyl derivative is shown to resemble that of ammonia, the final products being a pyrazolone derivative and ethylic malonate or benzylmalonate, the pyrazolone derivative being formed by condensation from the substituted amidoethylenedicarboxylate first produced. Phenylpyrazolone and several of its derivatives are described.

49. "*Action of Nitric Acid on Anthracene.*" (II.) By A. G. PERKIN and J. E. MACKENZIE (*Trans.*, 1892, 865).

One of the authors has previously shown that compounds of anthracene with either ethylic or methylic nitrates are formed when solutions of anthracene in ethylic or methylic alcohol are treated with nitric acid. It is now shown that the corresponding propylic, isobutylic, and benzylic compounds may be prepared by using the appropriate alcohols; no corresponding product could be obtained from trimethylcarbinol, the action of nitric

acid on the solution of anthracene in this alcohol giving rise to nitroanthrone.

Under slightly modified conditions, the action of nitric acid on anthracene dissolved in isobutylic alcohol is found to give rise to a compound which the authors regard as nitroanthrone,—



this is converted into the isomeric nitroanthrol by treatment with alcoholic potash.

On treating anthracene dissolved in acetone (Kahlbaum's pure) with nitric acid, the compound of anthracene with methylic nitrate was produced in such quantity as to negative the assumption that it was derived from methylic alcohol present in the acetone: it would therefore seem probable that the acid acts on the acetone forming methylic nitrate and acetic acid. Using methylated ether carefully freed from alcohol, the compounds of anthracene with both ethylic and methylic nitrate were obtained.

50. "The Behaviour of Ethylene on Explosion with Less than its Own Volume of Oxygen." By B. LEAN, B.A., and W. A. BONE, B.Sc. (*Trans.*, 1892, 873).

After giving a brief account of previous observations, the authors describe a series of experiments in which mixtures of ethylene with its own or a less volume of oxygen were fired in a leaden coil. Their results are in agreement with those of Dalton, Kersten, and E. von Meyer, and show that, when fired with about its own volume of oxygen, ethylene eventually yields mainly carbonic oxide and hydrogen; but they have also observed that methane, acetylene, and carbon are produced.

The following are the tabulated results of the analyses:—

Composition of mixture.	C.	D.	E.	F.	G.
Ethylene	56.03	54.18	49.77	48.64	49.41
Oxygen	39.46	41.52	45.81	45.84	47.69
Nitrogen	4.51	4.30	4.42	5.52	2.90
Composition of product.	C.	D.	E.	F.	G.
Unsaturated hydrocarbons	5.53	3.77	2.78	2.14	—
Methane	5.96	3.77	2.52	2.55	1.01
Carbon dioxide ..	1.63	2.80	1.24	0.94	0.33
„ monoxide ..	38.85	44.84	47.79	46.53	49.11
Hydrogen	43.30	41.72	43.32	45.35	48.78
Nitrogen	5.16	3.10	2.35	2.49	1.01

Incidentally it is shown that oxygen is appreciably absorbed by fuming sulphuric acid, but that neither strong potash nor alkaline pyrogallol solution appreciably affects ethylene.

51. "The Lowering of the Freezing-points of Cadmium, Bismuth, and Lead when Alloyed with other Metals." By C. T. HEYCOCK, M.A., and F. H. NEVILLE, M.A. (*Trans.*, 1892, 888).

The authors have considerably extended the inquiry of which they have previously given a short account (*Proc. Chem. Soc.*, No. 88). A very large number of data are recorded in the paper. From these it is apparent that the "atomic fall," i.e., the ratio of the fall in freezing-point of the alloy below that of the pure solvent to the number of foreign atoms present per 100 of solvent, is independent of the concentration when the solution is dilute. As the concentration increases, a gradual change takes place, however, in the atomic fall value. In a few cases, such as that of gold in cadmium or tin, and of mercury in cadmium, there is an increase in the atomic fall as the concentration increases, but in most cases the reverse is true.

The various possible causes of change in atomic fall with increasing concentration are considered, and, after calling attention to the fact that Van't Hoff's formula is strictly true only of infinitely dilute solutions, a formula applicable to finite concentrations is suggested; on the

assumption that the molecule of the substance in solution contains 1 atom, the different atomic fall values corresponding to different numbers of atoms of foreign metal per 100 of solvent are calculated, and it is then pointed out that on taking a general survey of the atomic falls given in the tables in the paper and comparing them with the molecular falls predicted by the theory of osmotic pressure, it is apparent, not only that the experimental numbers are identical in a great many cases with the theoretical fall produced by a monatomic molecule, but that the experimental numbers, while often lower, are never higher than the theoretical number. This is an important point in favour of the osmotic theory of solution, for this theory, whilst readily explaining a low atomic fall by the hypothesis of the dissolved molecule containing more than 1 atom, assigns a superior limit, corresponding to the state in which the molecules in solution contain each 1 atom of the dissolved substance. In presence of these numbers, it seems impossible to resist the conclusion that the process of dissolution consists essentially in the disintegration of the dissolved substance and its uniform diffusion through the solvent as a gas; in other words, that the "physical theory of solution" is correct. In some cases, however, for instance that of gold dissolved in cadmium and a few others, the authors have no doubt that the molecule in solution contains atoms of both metals.

52. "Isolation of a Compound of Gold and Cadmium." By C. T. HEYCOCK, M.A., and F. H. NEVILLE, M.A. (*Trans.*, 1892, 914).

The compound has the composition represented by AuCd , and is of a greyish silvery white appearance, like cadmium. It was prepared by alloying gold with cadmium and moderately heating in a vacuum so long as cadmium distilled away. The immediate interest of the compound is that it confirms the supposition advanced by the authors to account for the remarkable behaviour of gold and cadmium when dissolved in tin.

53. "The Resins of *Ficus rubiginosa* and *F. macrophylla*." By E. H. RENNIE, D.Sc., and G. GOYDER, Jun. (*Trans.*, 1892, 916).

An account is given of the results of an examination of the resins of *F. rubiginosa* by De la Rue and Müller, contained in a paper published in the *Phil. Trans.* of 1860, and the somewhat different results of the authors are then recorded. They have separated a crystalline substance from both resins externally closely resembling De la Rue and Müller's product, but giving numbers for carbon about 3 per cent, and for hydrogen about 1 per cent higher; the numbers are most in accordance with the formula $\text{C}_{34}\text{H}_{56}\text{O}_2$. This substance is resolved by alkaline hydrolysis into acetic acid and a crystalline substance melting at 114°, of the formula $\text{C}_{32}\text{H}_{54}\text{O}$, very closely resembling the substance described by De la Rue and Müller, which they obtained in a similar way.

54. "The Hydrolytic Functions of Yeast." Part II. By JAMES O'SULLIVAN (*Trans.*, 1892, 926).

A further series of experiments on the hydrolytic activity of healthy yeast cells are described, the following being a summary of the conclusions arrived at:—

1. The hydrolytic action of yeast at ordinary temperatures (12° to 20° C.) follows the same course as that of a simple chemical interchange, and is not influenced by either air or carbon dioxide.

2. A time curve representing the action would correspond with that given for invertase under the most suitable conditions of acidity by O'Sullivan and Tompson (*C. S. Trans.*, 1890, lvii., 878). The rate therefore differs from that at which the alcoholic fermentation of yeast takes place, which would be represented by a straight line (Dumas, *Ann. Chim. Phys.* [3], 1874, 81; and A. J. Brown, *C. S. Trans.*, 1892, 384).

3. Any interference involving either an increase or a diminution of the natural acidity of the yeast cell diminishes its action. This is a very important matter, and

should always be considered when dealing with organisms or cellular membranes possessing the power of hydrolysing cane sugar. Dumas observed that both acids and alkalis interfered with alcoholic fermentation, and that in the case of alkalis the yeast possessed the power of overcoming the alkalinity, the liquid again becoming acid, and fermentation recommencing. It is found that a quantity of potassium hydrate which completely arrested the hydrolytic action of yeast for three to six hours was neutralised by the yeast in about twenty-four hours, the solutions eventually becoming acid and hydrolysis recommencing.

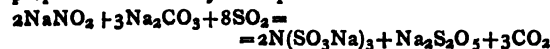
4. It is inferred from experiments on the effect of rupturing the cell on the velocity of the hydrolytic action, and also from the rate at which the change proceeds, that the whole of the invertase of the yeast cell comes into action as soon as the cane sugar is added to the yeast, and that it continues to act during the progress of the hydrolytic action.

5. The power which yeast possesses of producing alcoholic fermentation is not influenced by the yeast having first hydrolysed cane sugar, this being the case whether the hydrolytic action is brought about in the first instance in the presence of air or carbon dioxide.

55. "Imidosulphonates." By E. DIVERS and T. HAGA (*Trans.*, 1892, 943).

The authors have obtained sodium imidosulphonate for the first time, and from sodium nitrite by a modification of Fremy's method of preparing the corresponding potassium salt (sulphamidate). The potassium salt is nearly insoluble in water, but the sodium salt is exceedingly soluble; and whereas the direct preparation of the former has proved to be uncertain and the yield unsatisfactory, the latter can be obtained from the nitrite almost without loss. Probably the potassium salt could be much more easily prepared than it has been were the here described modified process adapted to its production; but the sodium salt is a much more useful agent because of its solubility, and the potassium salt can at once be prepared from it by precipitating with potassium chloride.

Sodium nitrite and sodium carbonate (crystals) in the proportions shown by the equation—



are placed in a flask together with a little water and a rapid stream of sulphur dioxide is passed into the magma. The flask needs to be agitated, and during the latter part of the process to be kept cool. When neutrality is approached, the gas is to be passed in more slowly, and is to be stopped just when lacmoid paper is first permanently reddened. Two salts are now present in the liquor, sodium nitrilosulphonate and metasulphite, but in a few minutes hydrolysis of the nitrilosulphonate sets in, giving disodium imidosulphonate and acid sulphate, and the latter acts on the metasulphite, forming sulphurous acid and disodium sulphate. By thus taking up the sulphuric acid, the metasulphite entirely prevents subsequent hydrolysis of the imidosulphonate into amidosulphonate. After expelling sulphur dioxide by a rapid current of air, a little sodium carbonate is added to make the liquor slightly alkaline, and enough of the water is evaporated off at a gentle heat. On cooling to near 0° , most of the sulphate crystallises and can be removed. The concentrated mother-liquor affords hard, brilliant crystals, of almost pure imidosulphonate; from its mother-liquor more sulphate and imidosulphonate can be alternately separated. The imidosulphonate can be safely re-crystallised from slightly alkaline warm water or by cold evaporation. It forms large, rhombic prisms of the composition—



feebly acid to litmus, which only very slowly lose water in a vacuum.

Like the potassium salt, disodium imidosulphonate is not precipitated by many of the ordinary agents, because

nearly all other imidosulphonates corresponding to it are soluble. It, however, affords precipitates with sodium hydroxide, potassium chloride or nitrate, barium hydroxide, strong ammonia-water, basic lead acetate, and mercuric and mercurous nitrates; most of these act also on the dipotassium salt. Sodium hydroxide precipitates trisodium imidosulphonate; and the same salt is formed by evaporating the disodium salt with sodium carbonate, or with sodium acetate if the evaporation is repeated. Potassium chloride precipitates the dipotassium salt. Ammonia precipitates a sodium ammonium salt, and also when the solutions are very concentrated triammonium imidosulphonate; but in presence of other sodium salts, nitrate or chloride, ammonia precipitates pure trisodium imidosulphonate, leaving ammonium nitrate or chloride in solution. Baryta-water gives a barium sodium imidosulphonate.

Trisodium imidosulphonate, $\text{NaN}(\text{SO}_3\text{Na})_2 \cdot (\text{OH})_2$, crystallises in thin plates, sparingly soluble in cold water, freely soluble in hot water. It is a very stable salt, easy to prepare and to preserve for unlimited periods. It is an alkaline salt, and when neutralised with sulphuric acid furnishes a solution from which the disodium salt can be crystallised out. In a vacuum the crystals lose only eleven mols. of water; the other one can be expelled by heat almost completely. A number of other imidosulphonates of corresponding composition, often double salts, can be prepared from the trisodium salt by precipitation; ammonium imidosulphonates can be also prepared from it, through the intermediation of the barium hydrogen salt, or the basic lead salt, or the silver salt.

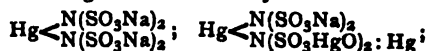
Berglund, eighteen years ago, established the fact that diammonium imidosulphonate is Rose's parasulphatammon, still described in the latest English text-books (Ramsay, Mendeleeff) as ammonium amidosulphonate. The authors find that dry diammonium imidosulphonate, an anhydrous salt, combines with dry ammonia to form anhydrous triammonium imidosulphonate, and that this is Rose's sulphatammon. They have also prepared in the wet way a triammonium imidosulphonate with 1 mol. of water, isomorphous with tripotassium imidosulphonate.

Barium imidosulphonate is precipitated as a voluminous matted mass of microscopic, fibrous crystals, in appearance like an organic salt. Barium hydrogen, barium ammonium, barium sodium, barium potassium imidosulphonates are all crystalline salts. Of the double calcium salts, the sodium compound may be mentioned as forming stellate groups of thick, often very brilliant, prisms.

Besides a very soluble, unstable lead hydrogen salt, a prismatic tri-hemihydroxy-lead salt, $(\text{HOPb})_3\text{N}(\text{SO}_3)_2$, and a tetra-lead salt, $\text{HO}(\text{HOPb})_4\text{N}(\text{SO}_3)_2$, which are both insoluble, may be obtained. No double lead salts can be prepared; the hydrogen salt is known only in solution.

The interaction of trisodium imidosulphonate and silver nitrate is specially remarkable for giving in succession three strikingly different precipitates:— $\text{AgNa}_2\text{N}(\text{SO}_3)_2$, in the form of fibrous, pale yellow crystals; $\text{Ag}_2\text{NaN}(\text{SO}_3)_2$, a sparkling, white "sand" of microscopic, hexagonal crystals, all detached; and $\text{Ag}_3\text{N}(\text{SO}_3)_2$, a white precipitate, drying on the tile to chalk-like masses. The relation in composition of these three silver salts is also interesting for its rare, if not exceptional, character.

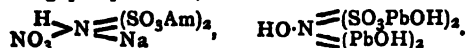
The following double mercury salts are well-defined compounds which have been examined in detail because of their interest as being at the same time sulphonic and nitrogen salts of mercury:—



Neither a single mercury imidosulphonate nor any mercurous salts can be prepared. Berglund's belief in the existence of a specially stable mercury imidosulphonic acid is not confirmed by the authors' observations, for although mercury dipotassium imidosulphonate readily

exchanges its potassium for barium and other metals, it keeps its potassium and exchanges its mercury for hydrogen when treated with nitric acid; and, besides, mercury hydrogen imidosulphonate is apparently less stable than imidosulphonic acid itself.

Diammonium imidosulphonate forms a double salt with sodium nitrate, and so does the dipotassium salt. The existence of these compounds and of the pentahydroxy-tetra-lead salt, and the retention of 1 mol. of water by the trisodium salt left in a vacuum-desiccator seem to show that imidosulphonates preserve some of the power of ammonia to unite with acids and salts, the nitrogen becoming quinquevalent, thus:—



The effect of heating ammonium and potassium imidosulphonates has been examined by previous workers, but their observations are defective. Diammonium imidosulphonate melts and boils near 357°, and flows back almost unchanged. Violent ebullition for an hour has little effect if moisture be rigorously excluded. But the salt decomposes to a small extent like the potassium salt. Dipotassium imidosulphonate is decomposed only at the softening point of good soft lime glass into potassium sulphate, ammonia, sulphur dioxide, and nitrogen. The carefully dried disodium salt behaves similarly. The trisodium salt at the same high temperature gives sodium sulphate, sulphur, and nitrogen. Lead, silver, and mercury salts are somewhat more easily affected by heat; in their case, besides products such as are above enumerated, mercury and even its sulphide, silver and silver sulphide, lead sulphide and sulphite are among the products. The barium salt decomposes explosively.

Anhydrous imidosulphonates of potassium or sodium, alone or with other metals, when heated to about 130° and upwards in ordinary air, slowly increase in weight and become acid, being hydrolysed by the atmospheric moisture. This fact is the more interesting in that at about the same temperature amidosulphonates, heated in dry air or in a vacuum, give off ammonia and become imidosulphonates, as was first observed by Berglund.

ADDENDUM.—*Oxyamidosulphonates*. Soon after the appearance of the authors' last paper (*Journ. Chem. Soc.*, lv., 765), which treated of *oxyamidosulphonates*, Dr. Raschig wrote to request them to state on his behalf that he agreed with their account of the decomposition of these salts by caustic alkali, and wished to withdraw his own statement which had been based on qualitative observations only.

56. "Modification of Beckmann's Boiling-point Method of Determining Molecular Weights of Substances in Solution." By JOJI SAKURAI.

The great experimental difficulty affecting Beckmann's well-known method is the exact determination of the boiling-points. A thermometer dipped into a boiling liquid always gives irregular readings, but this difficulty may be completely overcome by the method already described by the author in his paper on "The Determination of the Temperature of Steam Arising from Boiling

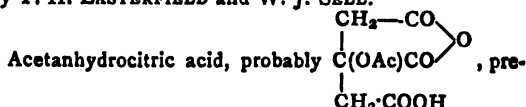
Salt Solutions" (*C. S. Trans.*, 1891), which consists in passing a current of the vapour of the solvent into the boiling liquid, the amount of the vapour thus passed in being regulated by the height of the lamp. The degree of constancy of the temperature attained in this manner by the boiling liquid is really astonishing, a most delicate thermometer capable of showing 1-1000th of a degree remaining almost stationary.

The apparatus used is of the simplest construction and can be set up by any one with materials commonly found in all chemical laboratories. Another advantage is that the boiling-point of the solution is ascertained just before its composition is determined, the connection between these properties being, therefore, rendered more certain than in the case of Beckmann's method.

The accompanying Table gives an example of the results obtained.

The author confirms the statement, first made by Beckmann, that the difference in colour of iodine when dissolved in ether and in carbon bisulphide is not due to a difference in the state of its molecular aggregation, the numbers obtained for the molecular weight of iodine, when dissolved in carbon bisulphide (247.1—261.9) agreeing with those contained in the Table (255.0—261.6). Beckmann's view that the molecular magnitude of sulphur in carbon bisulphide solution is represented by the formula S₈ has also received a striking confirmation in the author's hands, the numbers he obtained varying only between 252.3 and 254.9 (S₈=256).

57. "Anhydro-Derivatives of Citric and Aconitic Acids." By T. H. EASTERFIELD and W. J. SELL.



pared from anhydrous citric acid and acetic chloride, crystallises from ether in groups of short prisms melting at 115°; it decomposes at higher temperatures, yielding citraconic anhydride if distilled under ordinary pressure, and itaconic anhydride when distilled under reduced pressure (30 m.m.). It yields acetylcitric acid on hydrolysis; aniline converts it into citrodianilic acid; when hydrolysed by alcoholic potash it affords aconitic acid, the method being probably the best yet devised for the preparation of this acid. Ammonia converts acetanhydrocitric acid into citrazinic acid.

Aconitic anhydride may be prepared by boiling aconitic acid with excess of acetyl chloride; it crystallises out in colourless deliquescent octahedra. On treatment with ammonia it affords citrazinic acid.

The authors were unable to obtain citrazinic acid from tricarballic anhydride and ammonia, and point out that the formation of this acid from citric ethereal salts is probably largely dependent on the easy formation of an ethenoid union.

58. "Disubstituted Semithiocarbazides." By AUGUSTUS E. DIXON, M.D.

In two former papers (*Trans.*, 1889, 302; and 1890, 257) the author gave a short account of some members of

Solvent: Ethyl Ether.

Lat. Ht. Vap.=90.1 (Regnault, 1862); b. p.=34.9° C. $\frac{0.02T^2}{W} = 21.0$.

Substance.	B. p.			g solution.	g substance.	g solvent.	g substance per 100 g solvent.	Observed molecular weight.	Diff. per 100.
	Solvent.	Solution.	Rise.						
Salicylic acid, C ₆ H ₄ OH·CO ₂ H=138	1°13	1°397	0°384	6°9880	0°1733	6°8147	2°543	139.1	+0.8
" "	"	1°337	1°661	0°324	7°2700	0°1591	2°237	145.0	+5.1
" "	"	0°986	1°236	0°250	7°1384	0°1174	1°672	140.4	+1.7
Naphthalene, C ₁₀ H ₈ =128	0°739	1°464	0°725	7°2743	0°3128	6°9615	4°493	130.1	+1.7
" "	1°038	1°541	0°503	7°0014	0°2143	6°7871	3°159	131.9	+3.0
" "	1°275	1°542	0°267	7°0232	0°1112	6°9120	1°609	126.6	-1.1
Iodine, I ₂ =254	1°295	1°615	0°320	7°1600	0°2678	6°8922	3°886	255.0	+0.4
" "	1°098	1°302	0°204	7°2838	0°1796	7°1042	2°528	260.2	+2.4
" "	1°174	1°255	0°081	6°9250	0°0692	6°8558	1°009	261.6	+3.0

the class of semithiocarbazides, principally with reference to the isomerism there shown to exist amongst the di-substitution derivatives. The study has since been continued, but the publication of a paper dealing with such compounds was deferred until further investigation should be made regarding a phenomenon which was frequently observed, viz., the apparent existence, for a given semithiocarbazide of two different melting-points. A communication has, however, just appeared in the *Berichte* (1892, 3098), in which this latter subject is especially dealt with; the author, therefore, desires to record, without further delay, the experimental results which he has already obtained.

Paratolylphenylsemithiocarbazide (from p -ToNCS and $\text{PhNH}\cdot\text{NH}_2$) occurs as a colourless crystalline mass, sintering at 149° ; or in vitreous prisms, melting at 173° to 174° (uncorr.).

Phenylparatolylsemithiocarbazide (from PhNCS and p -ToNH $\cdot\text{NH}_2$) occurs as a crystalline mass, sintering at 117° , and convertible, by repeated crystallisation from boiling alcohol, into feathery needles, becoming electrical on friction and melting at 172° (uncorr.). This and the preceding pair are doubtless identical with compounds described (*loc. cit.*) by Marckwald.

Orthotolylparatolylsemithiocarbazide, when prepared at a moderate temperature from o -ToNCS and p -ToNH $\cdot\text{NH}_2$, melts at 130 – 131° , immediately resolidifying; on further heating, it again melts at 162 – 163° . The compound of m. p. 162 – 163° is directly obtained by combining the constituents in boiling (alcoholic) solution.

Paratolylorthotolylsemithiocarbazide, prepared from p -ToNCS and o -ToNH $\cdot\text{NH}_2$, forms vitreous prisms melting at 141 – 142° (uncorr.). The formation of a compound having a lower melting-point was not observed.

Diorthotolylsemithiocarbazide.—Brilliant colourless octahedra, melting at 148 – 149° (uncorr.).

Diparatolylsemithiocarbazide.—If prepared in gently-warmed alcoholic solution, forms aggregates of flattened crystals, melting at about 125° , but at once resolidifying and then melting at or near 153° . By mixing boiling alcoholic solutions of the constituents, the substance is obtained in pointed prisms melting at 153 – 154° (uncorr.).

Alphanaphthylphenylsemithiocarbazide (from α -NapNCS and $\text{PhNH}\cdot\text{NH}_2$).—Brilliant vitreous needles, melting at 183° (uncorr.). Isomeric with Freund's (*Ber.*, xxiv., 4790) phenyl- α naphthyl derivative melting at 135° .

Phenylbetanaphthylsemithiocarbazide, prepared from PhNCS and β -NapNH $\cdot\text{NH}_2$, forms pearly needles, melting at 184 – 184.5° (uncorr.). According to Freund (*loc. cit.*) this substance melts at 202° .

Betanaphthylphenylsemithiocarbazide, prepared from β -NapNCS and $\text{PhNH}\cdot\text{NH}_2$, crystallises in silvery needles, melting at 190 – 191° (uncorr.).

Benzylphenylsemithiocarbazide.—White flexible prisms; m. p. 115 – 116° (uncorr.). On heating in alcoholic solution with a trace of chlorhydric acid, the m. p. rises to 163° .

Benzylparatolylsemithiocarbazide.—Shining flattened prisms; m. p. 120 – 121° (uncorr.).

59. "Studies on the Interaction of Bromine and Toluene. Preparation and Properties of Ortho- and Para-bromotoluene, and of the Dibromotoluenes Derivable therefrom. Ortho- and Para-bromotoluenesulphonic Acids." By A. K. MILLER, Ph.D.

It is shown that parabromotoluene affords two dibromotoluenes, viz., orthoparadibromo- and metaparadibromotoluene, the latter being the major product; orthobromotoluene yielding orthoparadibromotoluene as minor product, together with the orthometa-derivative containing the bromine atoms relatively in the para position. Parabromotoluene also yields some 1:2:4:5-tribromotoluene ($\text{Me}=\text{I}$), which appears to be derived from the 1:2:4-di-derivative.

60. "Note on the Constitution of Neville and Winther's Orthotoluidinesulphonic Acid, and on the Acids Formed

by Sulphonating Orthochloro- and Bromo-toluene." By W. P. WYNNE, D.Sc.

A comparison of the chloro- and bromo-acids obtained by Sandmeyer's method from Neville and Winther's orthotoluidinesulphonic acid with those formed from orthochloro- and orthobromo-toluene by sulphonation has established their identity. Neville and Winther gave reasons for assigning to their acid the constitution $[\text{Me}:\text{NH}_2:\text{SO}_3\text{H}=1:2:5]$, but further evidence seemed desirable in view of the nature of their proof. The metabromotoluidinesulphonic acid formed from Neville and Winther's acid by careful bromination was converted by Sandmeyer's method into the corresponding dibromotoluenesulphonic acid, and the sulphonic radicle was eliminated from the acid by hydrolysis with phosphoric acid in a current of superheated steam; the resulting dibromotoluene was identified as the 1:2:3-derivative, since it melted at 30 – 31° , and its nitro-derivative at 59° .

It hence follows that the bromotoluidinesulphonic acid has the constitution $[\text{Me}:\text{NH}_2:\text{Br}:\text{SO}_3\text{H}=1:2:3:5]$, and Neville and Winther's acid that assigned to it by them.

61. "The Action of Iodine on a Mixture of Sulphite and Thiosulphate." By ARTHUR COLEFAZ, M.A., Ph.D.

This paper has reference to Spring's contention, advanced in his recent note in the *Proceedings* (1892, 91), that although it is true, as the author had asserted, that no trithionate is formed by the action of iodine on a mixture of sodium sulphite and thiosulphate, trithionate is produced if potassium salts are used in place of sodium salts. It is shown that trithionate is not produced by the action of iodine either on the potassium or sodium salts, and that the formation of trithionate is due to the occurrence of a secondary interaction of tetrathionate and sulphite, which takes place when the iodine acts slowly, as it does, especially when used in the solid state. It is also shown that when iodine acts on a solution containing both sulphite and thiosulphate of potassium or sodium, present in molecular proportions, it oxidises the sulphite only slightly more quickly than it converts the thiosulphate into tetrathionate.

62. "The Methylic Salts of Camphoric Acid." By JAMES WALKER, Ph.D., D.Sc.

The author has prepared the dimethyl and the two methyl hydrogen salts of camphoric acid, and finds their properties to be in the main the same as those of the compounds described by Brühl and Braunschweig and by Haller. Orthomethylic sodic camphorate may be obtained by adding 1 mol. prop. of powdered camphoric anhydride to a cold solution of 1 at. prop. of sodium (1 mol. prop. sodium methoxide) in methyl alcohol; the corresponding hydrogen salt may be prepared by acidifying the sodium salt. If 1 mol. prop. of methyl iodide be added in addition, and the mixture be heated for twenty-four hours at 100° , dimethylic camphorate is formed. The author succeeded in obtaining the allomethylic hydrogen camphorate in a measurable form by crystallisation from metaxylene. The "dissociation" constant of the ortho-compound is 0.00108, of the allo-compound 0.000975, which are nearly equal and not far removed from half of that of camphoric acid, viz., 0.00225. These values correspond with the assumption that camphoric acid is a dicarboxylic acid, and are at variance with the formula proposed by Friedel.

The Chemical Society.—We wish to draw special attention to the fact that an Extra Meeting of the Chemical Society will be held at 8 p.m. on Tuesday, December 13th, the Anniversary of the death of Stas. A paper, specially prepared for the occasion by Prof. J. W. Mallet, F.R.S., entitled "Jean Servais Stas, and the Measurement of the Relative Masses of the Atoms of the Chemical Elements," will be read and discussed.

NOTICES OF BOOKS.

Practical Physics: an Introductory Handbook for the Physical Laboratory. By W. F. BARRETT, F.R.S.E., M.R.I.A., and W. BROWN. Part I. "Physical Processes and Measurements, the Properties of Matter." 12mo., pp. 284. London: Percival and Co., 1892.

THE authors in their preface quote the important dictum of Prof. Huxley, that in Science "mere book-learning is a sham and a delusion." They eulogise the value of practical physics as mental discipline, and they applaud the "enlightened policy of the Director of the Science and Art Department" for doing what we should consider a simple duty.

It is noted that "the number of existing text-books in practical physics is still very small compared with the many admirable handbooks on practical chemistry." The authors surely do not consider this number of works to be any advantage! The introductory chapter, they think, may be objected to as going beyond the proper boundary of physics, and they suggest that teachers who are of this opinion may begin with Chapter II. The next chapters up to V. are intended for general students. Chapters VI. to IX. are more especially adapted for those who have the engineering phase of the subject in view, and the remaining chapters are intended for those taking up pure physics or chemistry.

In Chapter I. the authors "take up the hatchet" against the hypothesis of the evolution of atoms, which, in the words of Sir John Herschel and Prof. Clerk Maxwell, present the appearance of "manufactured articles." They omit, however, to show the raw material from which they have been manufactured. The idea of their being eternal and self-existent is more decidedly excluded by considerations drawn from their relative abundance and distribution.

Messrs. Barrett and Brown admit that temperature is not included "in any authorised way" in the three fundamental units—space, time, and mass. They do not deny the possibility of space of n dimensions. The more practical portion of the book, if duly taken in conjunction with experiments, will prove very useful for teachers and students.

Manual of Qualitative Blowpipe Analysis and Determinative Mineralogy. By F. M. ENDLICH, S.N.D., Mining Engineer and Metallurgist. 8vo., pp. 456. New York: The Scientific Publishing Co., 1892.

THE attention paid to blowpipe analysis in the United States is almost as striking as its comparative neglect in Britain. We might almost wonder that there should be an opening for the present work in face of the existing American version of Plattner. Dr. Endlich, however, does not enter upon the use of the blowpipe in quantitative operations. He devotes some pages to the application of the spectroscope in qualitative analysis, which he considers should be employed wherever possible. Its utility is, of course, not to be questioned. He gives also instructions for the examination of paints, pigments, and wall-paper. A number of methods for the determination of minerals are introduced which do not turn on the use of the blowpipe, but which will be found exceedingly useful. The general instructions for qualitative analysis are highly judicious, and speak of the habit of prolonged and careful observation. In Section 210 we observe a typographical error, the acidity of water on the absorption of sulphurous acid being said to produce *sulphides*.

In the table of atomic weights we find platinum given as higher than gold, the former being stated as = 196.7, and the latter as 196.2. In fine, though this work is not likely to supersede Plattner, it will prove a very useful adjunct, and it may be accordingly recommended to all chemists who practise blowpipe analysis, and of course to all mineralogists and metallurgists.

CORRESPONDENCE.

THE DETERMINATION OF PHOSPHORIC ACID IN BASIC SLAGS.

To the Editor of the Chemical News.

SIR,—I read with interest Dr. Adolf Jolles' criticism upon the Albert method of determining phosphoric acid in basic slags, which appeared in the *CHEMICAL NEWS*, vol. lxi., p. 262.

Having previously investigated the errors specifically shown by Dr. Jolles in his paper, I arrived at the same conclusions as himself, and communicated the results to others during the past year. I therefore feel sure of your permission to make a few comments upon the subject-matter of the German chemist's contribution.

I have no desire to make any untoward remarks upon Dr. Jolles' assertion, relative to the danger of missing some phosphoric acid through opening up basic slags with sulphuric acid, at the same time it would be rather a matter of surprise to find anyone experienced in the analyses of fertilisers adopting sulphuric acid as the solvent for these slags, which his comments seem to indicate.

Dr. Jolles rightly points out that the evaporation of the acid solution of slags to the consistency of a gelatinous paste is insufficient to effect the complete separation of silica. As a result of experiments made, I found that some silica invariably remains in solution, and that it was subsequently co-precipitated with the phosphoric acid, giving too high results as now described by him. It was therefore found necessary to evaporate the acid solution to absolute dryness in order to effect a perfect separation of silica, in some cases two evaporations being found preferable.

The condemnation of the Joulie volumetric method of estimating P_2O_5 by Dr. Jolles on account of the uncertain character of the prussiate indicator is justifiable, and I may say that I abandoned the use of this method several years ago when analysing raw phosphatic materials, finding it only possible to obtain approximate results even when the method was applied under conditions as far constant as possible as regards volume of liquid, quantities of salts present, &c.

The modification proposed by Dr. Jolles in the application of the Joulie method in the analysis of basic slags is requisite so far as regards too high figures, resulting from the incomplete separation of silica; but apart from this source of error, there is, I submit, reason to differ with Dr. Jolles in prescribing the Joulie method for the gravimetric determination of P_2O_5 . The writer has frequently observed the weight results obtainable by this method to be too high, and has found it to be untrustworthy for the accurate determination of phosphoric acid.—I am, &c.,

ALFRED FIRBY, F.I.C.,
Manure Analyst, &c

10, Infirmary Street, Leeds, Nov. 29, 1892.

DENSITY AND MOLECULAR WEIGHT.

To the Editor of the Chemical News.

SIR,—In making some calculations a few days ago, I noticed the following coincidence, which I take the liberty of communicating to you in case it might be of interest.

A gas doubles its volume when raised from 0° to 273° C.; greatest density of water is at 3.9° C. Now $273 + 3.9 = 276.9$ exactly; molecular weight of water = 17.96. Now $17.96 \times 3.9 = 70.04$, or $(3.9)^2 \times 17.96 = 273.18$, which is also freezing-point of water in absolute temperature. (Temperature of greatest density)² $\times$ molecular weight = 273.18.—I am, &c.,

H. TREHERNE.

THE VOLATILE FATTY ACIDS OF BUTTER.

To the Editor of the Chemical News.

SIR,—Will you grant me space in your next issue to deny Mr. Johnstone's statement that I made an arithmetical mistake in my "Note" (CHEMICAL NEWS, vol. lxxvi., 235)? My figures are all correct to the decimal to which they are calculated.—I am, &c.,

H. DROOP RICHMOND.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 21, November 21, 1892.

Action of Piperidine upon the Haloid Salts of Mercury.—Raoul Verdol.—The author has prepared piperidine chloromercurate and the corresponding bromomercurate, cyanomercurate, and iodomercurate. The mercurous chloride, bromide, and iodide, if treated with piperidine, are decomposed into metallic mercury and mercuric salts, which enter into combination with the base. If these results are compared with those previously obtained with ammoniacal gas and piperidine, it is found that at ordinary temperatures the haloid salts of mercury, if treated with an excess of these compounds, yield compounds containing 2 mols. of base to 1 mol. of salt of mercury.

Exchanges of Carbonic Acid and Oxygen between Plants and the Atmosphere.—Th. Schloesing, jun.—The question which the author undertakes to answer is what, for an entire plant during the whole term of its existence, is the result of the exchanges of carbonic acid and of oxygen which it effects with the ambient air? How much does it evolve for a given volume of carbonic acid which has disappeared? The experiments are described but no conclusions are reached.

Researches on the Method of Production of Perfume in Flowers.—E. Meunard.—The essential oil is generally localised in the epidermic cellules of the upper surface of the petals or the sepals. It may exist on both surfaces, especially if the parts of the flower are completely hidden in the bud. The lower surface generally contains tannin or pigments derived from it. 2. Chlorophyll seems in every case to give rise to the essential oil. The transformation is easily understood if we admit, as it is now generally done, that the parts of the flower are merely leaves modified for a new function. The chlorophyll is thus turned away from its object, and is transformed either into persistent tannin derivatives or into essential oils. 3. The development of the perfume of the flower is not perceptible until the essential oil is sufficiently liberated from the intermediate products, and it is present to some extent in an inverse proportion to the production of tannin and of pigments in the flower. This will explain why flowers with green petals have no odour; why white or rose-coloured flowers are most frequently odoriferous; why the Compositæ, which are rich in tannin, have their well-known disagreeable odour.

MISCELLANEOUS.

Diaries for 1893.—We have received from Messrs. Cassell and Co., Ltd., sole publishers of the original series of Letts' Diaries, a selection of the Rough and Commercial, and Office and Pocket Editions of Diaries for the ensuing year. These useful adjuncts to the desk and library are so well known that detailed comment is super-

fluous. We notice an addition to the No. 31 Rough Diary and the No. 8 Office Diary—the books most generally useful for offices—which cannot fail to be appreciated by many of our readers. It consists of copious extracts from the Telegraphic Code book known as the "Unicode." Here we have a selection of phrases likely to be required in ordinary business transactions, with the code word appertaining to the phrase. Thus, if we want to send the message "Leaving on the 20th by steamship; do not forward any more letters, keep them until my return," it is only necessary to send the two words "Inhumo, Mellis,"—an important saving in foreign telegrams where so much a word is charged. The information in the diaries is of a useful description and is generally up to date. In one of the diaries, however, the list of Her Majesty's Ministers is omitted "in consequence of the General Election taking place while going to press,"—a reason we should scarcely have expected from a firm like Messrs. Cassell's.

The American Philosophical Society, held at Philadelphia for the promotion of useful knowledge, has the honour to announce that it will celebrate the 150th Anniversary of its foundation by a series of reunions at the Hall of the Society during the week beginning Monday, May 22, 1893, terminating on Friday, May 26, 1893, at which papers may be offered by title by such members as may be present. The Society invites the participation of scientific men on this memorable occasion.—**Committee:** J. SERGEANT PRICE, RICHARD VAUX, DANIEL G. BRINTON, WILLIAM V. KEATING, FREDERICK FRALEY (*ex-officio*), HENRY PHILLIPS, JUN. (*Chairman*).

MEETINGS FOR THE WEEK.

- MONDAY, 12th.—Society of Arts, 8. (Cantor Lectures). "The Generation of Light from Coal-Gas," by Prof. Vivian B. Lewis. Medical, 8.30.
TUESDAY, 13th.—Institute of Civil Engineers, 8. Chemical, 8. (Extra Meeting on the Anniversary of the death of Stas). "Jean Servais Stas, and the Measurement of the Relative Masses of the Atoms of the Chemical Elements," by Prof. J. W. Mallet, F.R.S. Royal Medical and Chirurgical, 8.30. Photographic, 8.
WEDNESDAY, 14th.—Society of Arts, 8. "The Utilisation of Niagara," by Prof. George Forbes, F.R.S. Pharmaceutical, 8.
THURSDAY, 15th.—Royal, 4.30. Chemical, 8. Ballot for the Election of Fellows. "The Identity of Caffeine and Theine," by W. R. Dunstan and W. F. J. Sheppard. "Studies on Isomeric Change, 1:2:3-Orthoxylylene Sulphonic Acid, and Phenetolsulphonic Acid," by Dr. Moody.
FRIDAY, 16th.—Quekett Club, 8.

TO CORRESPONDENTS.

G. W. Blythe.—(1) Consult any elementary text-book on chemistry. (2) It cannot be bought. (3) Anhydrous ammonia is kept and sold under pressure in strong steel cylinders.

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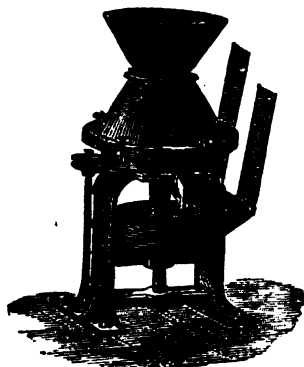
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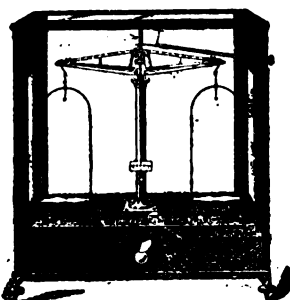
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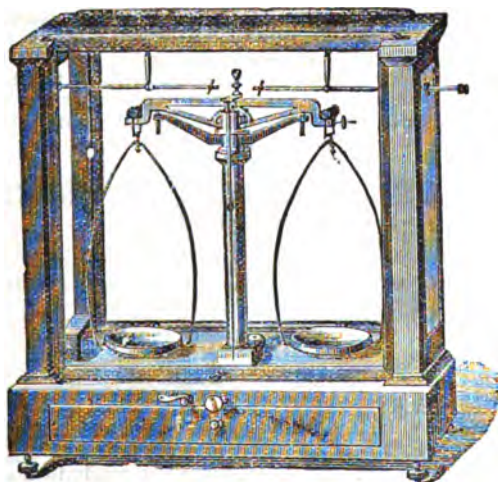


FIG. 3A.

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The process must be effected in a silver crucible, carefully observing the precautions given, so that the crucible may not be too much attacked, and a contamination of the melt with silver may be avoided as far as possible.

Ziegler uses a silver crucible holding about 50 c.c., and weighing from 45 to 46 grms. It must be heated with a reducing (smoky) flame, for which purpose the two air-holes of a Bunsen burner provided with a chimney are pasted over with paper, and very little air is admitted into the burner space by perforating the paper. During melting the crucible must be kept sooty.

For the analysis of ferrochrome $\frac{1}{2}$ gm. of the sifted sample is placed in the silver crucible and 6 grms. of chemically pure sodium hydroxide and 3 grms. of chemically pure sodium nitrate are added. The crucible is allowed to become sooty, and is heated with a rather small reducing flame, which is slowly increased. In about half an hour the process is complete if properly managed. When the contents of the crucible are cold (having been allowed to spread over the interior of the crucible shortly before congealing), it is placed in a porcelain capsule and filled up entirely with water. The solution may be expedited by stirring with a platinum rod.

When the salts are dissolved the contents are poured out, the crucible is wiped out and rinsed with water. The total liquid with the residue of ferric oxide is put into a beaker and is saturated with carbonic acid for half an hour. The entire mass is then evaporated to dryness in a porcelain capsule on the water-bath, dissolved in water and filtered. It is washed out with water containing a little sodium carbonate.

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* From the *Zeit. Anal. Chemie*.

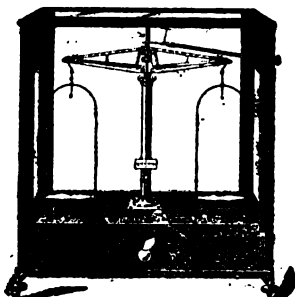
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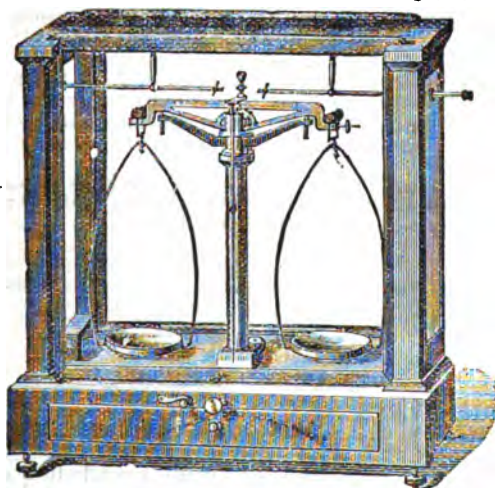


FIG. 34.

SHORT BEAM BALANCE, Fig. 32, No. 122, to carry 2000 grains in each pan, sensible to 1-300th grain. Agate bearings, one rider apparatus. Nickel pans, 3 in. diameter... £7 6 0
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Silicon is most simply determined by opening up $\frac{1}{2}$ gm. of the substance with sodium bisulphate at a moderate

* From the *Zeit. Anal. Chem.*

heat, as at very high temperatures basic sparingly soluble sulphates are formed.

Rud. Namias, who uses bisulphate for opening up ferrochrome, adds, when the opening up is completed, a little more bisulphate, which, however, is unnecessary unless too strong a heat has been applied. If the process has been properly conducted the melt dissolves as good as completely (except the silica) in hot water acidulated with sulphuric acid on a longer or shorter digestion; an addition of hydrochloric acid, as Namias proposes, being unnecessary. The silica thus obtained is never chemically pure, and must for the sake of accuracy be evaporated down with hydrofluoric acid. The filtrate from the determination of silica may be used for titrating the manganese.

For determining the phosphorus Ziegler takes 2 grms. of the sample, which he opens up with 9 grms. soda saltpetre and 18 grms. potassium hydroxide. The melt is taken up with nitric acid and a little hydrochloric acid converted into a nitric solution by repeated evaporation with concentrated nitric acid, neutralised with ammonia, and the phosphorus determined as usual. The sulphur can also be determined with the same melt.

The weighed chromic oxide, if tested with a saltpetre soda melt is almost always free from iron and manganese. Any trace of silicon in the chromic oxide, except that due to the filters, can be detected by fusion with sodium bisulphate, since the chromium oxide is thus completely converted into soluble sulphate.

Ziegler points out that according to an earlier process salts of chromic oxide in a sulphuric solution can be converted into chromates by permanganate, and then determined volumetrically with ferroammonium sulphate. According to the author this process, if slightly modified, yields good results.

The sulphuric solution of ferrochrome obtained by opening it up with sodium bisulphate can be advantageously oxidised with permanganate. The manganese hydroxide is free from chrome, and the precipitate of iron and manganese obtained with sodium carbonate contains only minimum quantities of chrome.

(To be continued.)

VOLUMETRIC DETERMINATION OF SULPHURIC ACID BY THE CHROMATE METHOD.

By K. FARNSTEINER.

THE author heats the solution, slightly acidified with hydrochloric acid, almost to ebullition, and precipitates it with a measured excess of a solution of barium chloride of known strength. It is heated for some time longer, ammonia free from carbonic acid is added until the reaction is faintly alkaline, and the excess of barium chloride is then precipitated by means of a measured volume of potassium chromate of known power of reaction. When cold, the liquid (which now contains only a slight excess of potassium chromate), is transferred along with the precipitate into a suitable measuring flask, which is then filled up to the mark, well shaken up, and after the precipitate has subsided half the liquid is filtered off. It is then mixed with potassium iodide and hydrochloric acid, either in a beaker or in a wide-necked flask capable of being closed with a glass stopper. After some minutes the eliminated iodine is determined with a solution of sodium thiosulphate.

For the calculation the strength of the solution of barium chloride must be exactly known, as also the relation of the solution of chromate on the one hand to the solution of barium chloride, and on the other to the solution of sodium thiosulphate.

This method, however, does not give useful results for

large quantities of sulphuric acid, as both the barium sulphate and the barium chromate carry down potassium chromate. For the determination of small quantities of sulphuric acid (0.02 to 0.04 gm. SO_3), the method, according to the author, may be recommended, especially if ammonium chromate is used instead of potassium chromate. The method is suitable for the determination of sulphuric acid in soda, in common salt, potash, and potassium chloride, as also for ordinary water. Of this from 100 to 200 c.c. are heated with a little dilute hydrochloric acid to decompose the carbonates, and the sulphuric acid is precipitated with barium chloride. The liquid is then made very slightly alkaline with ammonia free from CO_2 , the solution of chromate is added, proceeding further as above.—*Zeit. Anal. Chemis and Chem. Zeitung.*

A PROCESS FOR THE QUANTITATIVE SEPARATION OF SILVER AND LEAD.

By R. BENEDICT and L. GAUS.

THE authors found their process on the different behaviour of silver and lead iodides with dilute nitric acid.

The solution containing silver nitrate and lead nitrate—in all about 0.5 gm. of metal—is diluted with cold water in a capacious glass capsule to from 200–300 c.c., and solution of potassium iodide more than sufficient for the complete precipitation of the silver, but not excessive in quantity, is allowed to flow in. If 0.5 gm. of metal is used, 10 c.c. of a 10 per cent solution of potassium iodide will be sufficient in any case. We then add 10 c.c. of nitric acid free from chlorine, previously diluted with from 10–20 c.c. of water. The capsule is then covered with a watch-glass and heated on the water-bath, when the yellow colour of the precipitate chiefly passes at first into orange-red.

As soon as the liquid has become hot, the lead iodide dissolves, the liquid becomes dark brown, and vapours of iodine are given off. The watch-glass is then removed and rinsed into the capsule, boiling water is added, and the capsule is left on the water-bath, adding water from time to time to compensate for the loss by evaporation until the liquid has become colourless or pale yellow, when the iodine is expelled. The silver iodide is then weighed. The authors collect it in a small glass tube filled with glass wool, dried at 110° , and weighed. Wash it first with hot water containing nitric acid, and then with a few c.c. of hot water, dry at 110° and weigh.

The presence of other metals of the same group, with the exception of mercury, does not interfere. Cuprous iodide, bismuth, and cadmium iodide behave with nitric acid like lead iodide; on the other hand, mercurous iodide is converted into red iodide, which is not further attacked.

The authors publish very favourable results. In the examination of alloys of lead and silver they proceed in the same manner. They dissolve in nitric acid, dilute, precipitate with potassium iodide, and heat on the water-bath.

For determining silver in impure leads, from 10–50 grms. of the same, according to the proportion of silver, is dissolved in dilute nitric acid containing tartaric acid. To 10 grms. of the sample they use 10 c.c. nitric acid free from chlorine, and an equal quantity of a saturated solution of tartaric acid. The presence of the latter effects much more rapid and complete solution. The solution is heated until the oxidation is completed, diluted with boiling water, filtered into a glass capsule, diluted to from 300–500 c.c., allowed to cool, 10 c.c. of a 10 per cent solution of potassium iodide are added, and it is heated on the water-bath.

The excess of the nitric acid added for solution is

generally sufficient for oxidising the lead iodide; if the development of iodine vapours and the brown colour do not appear, a little more dilute nitric acid must be added.

The proportion of silver in galena may be determined in the same manner. It is oxidised with nitric acid with the addition of tartaric acid. It is most convenient to use equal volumes of nitric acid, solution of tartaric acid, and water. After the oxidation is completed, the liquid diluted with hot water, filtered, and well washed with boiling water, the filtrate is allowed to cool. The process is then completed as above.—*Zeit. Anal. Chemis und Chem. Zeitung.*

PHOSPHORIC ACID IN BERYL.

By FRANKLIN C. ROBINSON.

SEVERAL years ago (spring of 1883) Prof. J. Torrey, jun., now of the Harvard Laboratory, then a student in Bowdoin, found a mineral in the neighbouring town of Yarmouth which was of such peculiar appearance that I suggested that an analysis be made. Its appearance suggested a beryl; that is, it was of the well-known beryl form, but had hardly the suggestion of green colour and the crystallisation was rather indistinct. His analysis gave silica lower and alumina higher than they should be in beryl, and in addition phosphoric acid and alkalis were discovered to the amount of several per cent. Our notes, made at the time, show that while sodium and potassium were the chief alkalis in amount, undoubted traces of lithium and caesium were also present.

Our decision then was that the mineral was probably not a beryl, and it was laid aside for future work. Since then, as is well-known, other observers have proved the general presence of alkalis in beryl, and I have only awaited a favourable opportunity to re-examine the specimen and see if, after all, our first impression as to its being a beryl may not have been correct. My assistant, Mr. C. H. Cutts, has now made such re-examination with the following results:—

Colour, grey to white, with mere trace of green.
Hardness, 7. Specific gravity, 2.627. Loss on drying at 100° C., 0.33 per cent.

Loss on ignition		1.53 per cent.
Silica		64.70 "
Alumina		17.76 "
Beryllium oxide		12.18 "
Phosphoric acid		2.76 "
Alkalis (Na ₂ O, K ₂ O, Li ₂ O, Cs ₂ O)		1.10 "

100.03

Regarding the phosphoric acid and alkalis as replacing a part of the beryllium, we have the numbers 1, 2, 6, 12, for water, alumina, beryllium oxide, silica, respectively, showing that the mineral is really a beryl. The former low result in silica was not obtained owing to greater care in selecting a pure specimen for analysis.

The presence of phosphoric acid in this led me to have it tested for in other specimens of beryl, with the result that its presence has been detected in nearly every case; but in no other specimen has so large a percentage been found. I am unaware that any notice of the fact that phosphoric acid is frequently present in beryls has before been published.—*Journal of Analytical and Applied Chemistry*, vi., No. 9.

The Functions of Hydurilic Acid. Preparation of Potassium Hydurilates.—C. Matignon.—Hydurilic acid is tribasic. It possesses three different acid functions. The first comparable to the strongest acids of organic chemistry; the second of the same order as that of the normal carboxylic acids, and the third inferior to the feeble function of phosphoric acid.—*C. R.*, cxv., No. 22.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 1st, 1892.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

DRS. WILLIAM J. MCKERROW, John Shields, James Walker, and W. P. Wynne were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John Edwin Brockbank, The Croft, Kirksanton, *vid* Carnforth; Edward Brooke, West Court, Chalk, Gravesend, Kent; Charles Dreyfus, Ph.D., Clayton Aniline Co., Clayton, Manchester; James Elias, Briton Ferry, Glamorganshire; Alexander Stanley Elmore, Twaite Gate, Leeds; George Neville Huntly, 56, Sheen Road, Richmond, Surrey; Charles M. Luxmore, B.Sc., 529, Battersea Park Road; Robert Henry Owen, Pas-y-coed, Troedyrhiw, near Merthyr Tydfil; John William Towers, Brantwood, Allerton, near Liverpool; William Ernest Wheeler, Cumberland House, Meynell Road, South Hackney.

Of the following papers those marked * were read:—

*70. "The Isolation of Two Predicted Hydrates of Nitric Acid." By S. U. PICKERING.

In the case of nitric acid the curves plotted from both Berthelot's and Thomsen's heat of dissolution values were found to exhibit a well-marked "break" at the composition of the trihydrate; Kolb's density values afforded a similar indication, and also exhibited a "break" at the monohydrate; on making a series of freezing-point determinations, both these hydrates, but no others, were isolated in the crystalline condition. The melting-point of the trihydrate is -18.2°, and that of the monohydrate -36.8°. In the case of each the melting-point is lowered by the addition of either acid or water. These results are regarded by the author as an important confirmation of the views expressed by him in previous papers.

*71. "Anhydrous Oxalic Acid." By W. W. FISHER M.A.

Although the crystallised dihydrated acid is a familiar substance, anhydrous oxalic acid is but little known, except as a roughly dried mass, probably because it so readily attracts moisture. E. Reichert has shown that it is obtained from the hydrate by treatment with concentrated sulphuric acid (*Vena Zeit.*, 1864, vol. i., p. 244), but he states that the excess crystallising from a heated mixture of the two substances is a hydrate; this, however, appears to be an error. A. Villiers, in 1880 (*Compt. Rend.*, xc., 821), published a note on the crystals obtained by this method, and pointed out that they were of greater relative density than sulphuric acid. The crystalline form of the anhydrous acid has been described and figured by Löschmidt (*Wien. Akad. Ber.*, 1865), but owing to the readiness with which the crystals change in air, the determinations were but approximate; they are prismatic octahedra, resembling elongated crystals of alum.

The best method of producing the crystals is to allow ordinary hydrated oxalic acid to remain in contact with concentrated sulphuric acid for a few months; if the two substances are sealed up together in a glass tube, beautiful specimens may be obtained. Oxalic acid, whether hydrated or not, is sparingly soluble in sulphuric acid, about 3 per cent being taken up by the cold liquid. The anhydrous acid dissolves with a slight fall of temperature, while a rise of temperature is noticed when the hydrated crystals dissolve. Dissolution takes place readily on warming, and part of the dissolved acid separates in the anhydrous state on cooling the solution, a supersaturated liquid being obtained from which the excess is slowly deposited.

The relative density of the crystals, determined in dry petroleum, was found to be 1.878 compared with water at 4°, while the density of the hydrated acid similarly determined was found to be 1.608 (Bödeker, *Fahresb.*, 1860, 17, gives $d=2.0$). This difference affords a ready means of distinguishing the hydrated crystals, as when placed in concentrated sulphuric acid they at first float, but losing their transparency and turning white as they become dehydrated, they increase in density and finally sink to the bottom.

The limit of concentration at which crystallised oxalic acid in contact with sulphuric acid retains its water is between 60 and 70 per cent at ordinary temperatures, as the hydrated form is unchanged in the weaker acid and the anhydrous crystals are permanent in the 70 per cent sulphuric acid.

Hydrated oxalic acid behaves in a similar manner towards nitric acid, as it may be re-crystallised from that containing about 70 per cent of real acid ($d=1.2$) without losing its water, while in a highly-concentrated acid ($d=1.50$) it is dehydrated.

The crystals deposited from nitric acid are usually less brilliant in appearance and smaller than those formed in sulphuric acid.

Commonly, oxalic acid is dried by the rough method of heating in an open dish, when a considerable part of the water is expelled, but much loss takes place by volatilisation, and unless the acid be actually sublimed the drying is still imperfect. It can, however, be easily and completely dried in a vacuum by means of the arrangement described by McLeod (*C. S. Trans.*, 1883, 384) or in an ordinary retort; for this purpose the retort containing the acid is attached to a receiver containing strong sulphuric acid, exhausted by a water vacuum pump, and heated at 60° on a water-bath; in a few hours the theoretical quantity of water is expelled from the crystals.

A specimen dried in this manner, which had been transferred to a tube, then sublimed in a vacuum by a steam heat and sealed up in the year 1890, appeared in the ordinary form of the sublimed acid as a mass of needles, but after a few months, by slow re-sublimation at ordinary temperatures, the interior of the tube became coated with brilliant crystals resembling those deposited from sulphuric acid.

The volatility of hydrated oxalic acid was observed by Faraday (*Journal Royal Institution*, 1830), who found that when kept in an open tube for four years within a stoppered bottle containing calcium chloride, some oxalic acid passed over into the calcium solution, and new crystals were visible on the surface of the old ones. The hydrated acid does not appear to sublime as readily as the anhydrous form, specimens enclosed in vacuous tubes showing, after several months, hardly any signs of volatility.

The stability of oxalic acid is evidenced by the fact that it can be readily sublimed in a vacuum at temperatures up to 150; and that, even if heated on the water-bath in concentrated sulphuric acid, a portion will sublime from the liquid undecomposed.

Anhydrous oxalic acid will dissolve in warm ethylic oxalate or glacial acetic acid, but does not crystallise well from either solvent, only a powdery product being obtained.

*72. "The Production of Orcinol and other Condensation Products from Dehydracetic 'Acid.'" By N. COLLIE, Ph.D., and W. S. MYERS, B.Sc.

Oppenheim and Precht have stated (*Ber.*, 1876, 324) that orcinol is formed when dehydracetic "acid" is hydrolysed by means of barium hydrate, but they obtained only a very small quantity, and based their conclusion on qualitative evidence; their observation is now corroborated by the authors, who have obtained orcinol, not only from dehydracetic "acid" and dimethylpyrone by the action of barium hydrate, but also by boiling a mixture of syrupy caustic soda and dehydracetic "acid"; in the

latter case a true (carboxylic) acid is first produced, which loses carbon dioxide, leaving orcinol.

Among the products obtained on submitting diacetylacetone to the action of barium hydrate, the authors have discovered a substance crystallising in bright yellow needles melting at 180—181°, which is probably a naphthalene derivative, its formation involving the change expressed in the equation $2C_7H_{10}O_3 = C_{14}H_{14}O_3 + 3H_2O$. Mention is also made of a substance exhibiting a magnificent blue fluorescence formed in the preparation of diacetylacetone from dimethylpyrone by treatment with baryta water.

An amidodehydracetic "acid" is described, which is formed by the interaction of solid dehydracetic "acid" and the strongest ammonia solution; it crystallises in long silky needles, m.p. 192—196°, and is readily re-converted into dehydracetic "acid" by alkaline or acid hydrolysis.

*73. "Observations on the Origin of Colour and on Fluorescence." By W. N. HARTLEY, F.R.S.

Adverting to the arguments used by Armstrong in the *Proc. Chem. Soc.*, 1888, iv., 27, the author defines colour and the cause of colour, the nature of visible and invisible colour, and the limits of visibility in the spectrum from a physical standpoint. It is contended that it cannot be stated in general terms that colour is due to special modes of atomic arrangement, but that the statement may be applied in a restricted sense to certain carbon compounds, especially to those included in the class to which organic dye-stuffs belong; and it is pointed out that all open chain hydrocarbons exert a continuous absorption, the extent of which depends on the number of carbon atoms in the molecule.

Attention having been drawn by Armstrong to the condition of strain and of instability existing in many coloured substances, it is pointed out that this is owing to their being all endothermic compounds; that ethylene, acetylene, and benzene are endothermic, but that derivatives of the last-named only are coloured; and finally that all organic colouring matters are endothermic compounds.

This is considered to be the physical cause of that which Armstrong has not defined, but which he terms "reactivity" or "high potential."

It is next shown that anthracene is not colourless, but has a true greenish yellow colour in addition to its fluorescence.

The results of a number of experiments on fluorescence are then given in detail, and from these the following conclusions are drawn:—

1. Quinine dissolved in alcohol exhibits a beautiful bright violet fluorescence.
2. Chlorhydric acid is not fluorescent.
3. Quinine hydrochloride is very feebly fluorescent, but without distinct colour.
4. Chloroform is feebly fluorescent, but without distinct colour.
5. Both chlorhydric acid and chloroform can extinguish those rays which are the cause of the fluorescence in quinine.
6. Some alkaloids may be recognised by the degree and colour of the fluorescence they exhibit.
7. Normal alcohols of the ethylic series are fluorescent; so, also, are the fatty acids.
8. Glycerol has a violet fluorescence.
9. Benzene has a pale blue fluorescence, azobenzene a greenish blue.
10. Rock crystal has a pale bluish-violet fluorescence, flint glass a strong blue, and crown glass a very brilliant and beautiful blue fluorescence.
11. Substances which are not fluorescent in strong solutions may become so on dilution, particularly if they exert a very powerful absorption of the ultra-violet or visible spectrum.

The colour and fluorescence of anthracene are ex-

plained. Finally, the case of ortho- and para-nitrophenol and of meta- and para-nitraniline are discussed, and it is contended that the formulæ of ortho-nitrophenol and metanitraniline should not at present undergo modification.

*74. "The Origin of Colour. (V.) Coloured Hydrocarbons and Fluorescence: a Reply to Prof. Hartley's Observations on the Origin of Colour and of Fluorescence." By HENRY E. ARMSTRONG.

A perusal of my friend's objections leaves me under the impression that he scarcely apprehends my views on the origin of colour, and that he does not fully comprehend my aim; but this is not surprising, my arguments having hitherto been published in the briefest and most condensed form, as I have always felt that, in dealing with so difficult and extensive a subject, it was necessary to proceed slowly, and to read, mark, learn, and give much time for inward digestion and further experimental study before venturing to discuss in detail the manifold issues involved. My critic having clearly accentuated many of the points which demand consideration, I am in consequence much indebted to him; moreover, the fact that he has paid special attention to the study of ultra-violet absorption-spectra lends great weight to his statements, which serve also to indicate the departure from current views involved in the adoption of the hypothesis of which I am an advocate. I have never left out of account the fact that, in a physical sense, all substances are coloured—all substances possessing the power of absorbing the light waves, either generally or selectively, in some part either of the visible or invisible spectrum. My contention has been simply that, confining our attention to visibly coloured organic substances to substances coloured in the ordinary conventional sense, it is a most remarkable fact that in those cases in which the "constitution" of the coloured substance is fairly well established, coloured substances are all of one type, and from this base I have started on the inquiry whether all coloured organic compounds are not similar in type.

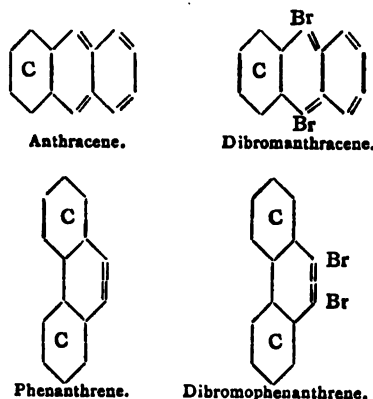
According to Hartley, "in order to study the origin of colour, we must first consider the case of colour in those molecules which are of the simplest possible constitution, such as, for instance, the molecules of chlorine, oxygen, ozone, and water." Undoubtedly this would be the case if we knew their "constitution"; but we do not, our knowledge being confined to the fact that their molecules consist of a certain number of atoms—which is insufficient. He also asserts that "the colour or effect on light caused by molecules of oxygen, ozone, and water, is in no way different from that caused by molecules of aniline blue." This may or may not be a correct interpretation of the facts; apparently the molecules of both oxygen and ozone are intrinsically coloured, but is the water molecule? It is an important question for experimental investigation whether water in a perfectly gaseous state would be blue when viewed in a column of sufficient thickness; its colour may originate in the poly-molecules which presumably are contained in the liquid.

My critic furthermore states that "all organic colouring matters are endothermic compounds." This may well be the case, but the converse does not hold, as he himself recognises, and the conclusion helps us but little; such a phrase, in fact, serves but to obscure the issue by merging the less in the greater.

A most important section in the paper under notice is that relating to fluorescence, describing a series of observations which lead their author to conclude that many substances are fluorescent which hitherto have not been considered to be so, e.g., alcohol and its homologues, &c. There can be no question as to the accuracy of these observations, but until many of the substances have been further studied, and every possible precaution has been taken to obtain them *pure*, I must, with all deference, decline to accept all the results as final. In the case of naphthalene derivatives, especially the naphthyl-amine and naphthol-sulphonic acids, with which I am somewhat

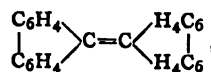
familiar, intensely fluorescent solutions are the rule—yet I very much doubt their being fluorescent, having noticed time after time, that the more nearly pure the substance becomes, the less fluorescent it is. It is easy also to account for the presence of fluorescent impurities in these cases on the assumption that during the heating with sulphuric acid oxidation takes place, and that the resulting phthalic acid, or nearly allied compound, condenses, forming a fluorescein; a strong argument in favour of this explanation is afforded by the fact that the disulphonic acids which are formed with the aid of fuming acid at somewhat elevated temperatures, and are very soluble, and therefore difficult to purify, are far more strongly fluorescent than the monosulphonic acids, which are difficultly soluble and comparatively easily purified.

In considering the "origin of fluorescence" and in regarding it as the "beginning of colour," I am, undoubtedly, entering into a highly speculative region; yet the facts are very striking. A single example will suffice. Anthracene is intensely fluorescent, and it may be represented by a quinonoid formula; the isomeric hydrocarbon, phenanthrene, however, which cannot be so represented, is colourless and non-fluorescent, according to present knowledge. Hartley's discovery that anthracene has a visible slight greenish yellow colour is to me one of extreme interest, and I cannot refrain from referring to it as a very strong confirmation of my hypothesis. Furthermore, while an intense yellow colour is produced by "weighting" what may be termed, for convenience, the "quinonoid radicles" of anthracene by introducing chlorine or bromine in place of the central hydrogen atoms, no such effect follows the introduction in a similar manner of bromine into phenanthrene, dibromophenanthrene being colourless like the hydrocarbon. And yet anthraquinone and phenanthraquinone are both coloured, the latter being deep orange and the former yellow.



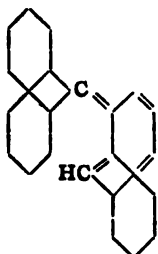
Much more evidence of this character might be adduced, but I have said sufficient to show why Hartley's arguments have not shaken my conviction that we may eventually be led to regard fluorescence as a feeble manifestation of that which we ordinarily describe as colour.

While speaking of anthracene as a coloured hydrocarbon, reference may be made to other coloured hydrocarbons, of which we now know several, viz., carotin, and the red hydrocarbon, $C_{26}H_{16}$, obtained by van Dorp and de la Harpe by passing fluorene over heated lead oxide, which has recently been investigated by Graebe (*Ber.*, 1892, 3146). We know nothing of carotin at present. Graebe represents the hydrocarbon from fluorene by the formula—

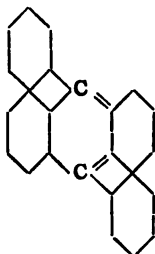


and therefore terms it dibiphenylenethene; I venture to suggest that it would be more appropriately named *Ery*.

throphene, a term which does not commit us to any definite view as to its constitution. I have no hesitation in asserting that a hydrocarbon represented by the formula proposed by Graebe would be colourless, and I would suggest the formula given below as more probable; at the same time it may be pointed out that the yellow hydrocarbon $C_{26}H_{14}$ (*xanthophene*), which van Dorp and de la Harpe obtained together with "erythrophene," may be a diphenylenated anthracene.



Erythrophene.



Xanthophene.

Both hydrocarbons are represented by quinonoid formulæ and the "quinonoid radicles" are heavily "weighted"; hence they are somewhat intensely coloured.

As to the nitrophenols, I have not called in question the constitution of the ortho-compound simply because it has a yellow colour; I have also pointed out that it differs in many other respects in a marked manner from its isomerides. Hartley's remarks appear to me in no way to affect my argument. With reference to the nitro-compounds, he states that "a very little shifting of the region of absorption to rays a little more or a little less refrangible, makes such substances colourless or coloured." No doubt this is so, but the question I would raise is whether the shifting necessary for the production of visible colour (and in a measure of fluorescence) is not conditioned by a special character of structure. In such a case as that of diorthonitrophenol, for example, which is yellow and affords intensely red metallic derivatives, yet yields colourless ethers, it is very difficult to avoid the conclusion that this is so; if we consider the propyl and potassium derivatives, the change from colour to colourlessness, or *vice versa*, cannot be conditioned by a change in "weight" of the radicles, as they are so nearly alike in this respect; Hartley, I imagine, would attribute the difference to the higher "energy" of the metallic radicle, but this latter idea is also, in a measure, included in my suggestion that colour in such a case is developed as a consequence of an isodynamic change, and it must not be forgotten that the evidence of changes of this character occurring is rapidly increasing in volume, e.g., Perkin's recent observations on the magnetic rotation of compounds supposed to contain acetyl.

Hartley's explanation of the non-fluorescence of quinine hydrochloride—that it is due to the absorption by the hydrogen chloride solution of the very rays which are the cause of the fluorescence in quinine—is both simple and satisfactory, and I have no hesitation in accepting it; but this in no way alters my conviction that the fluorescence of quinine itself is in all probability conditioned by peculiarity of structure.

Finally, I do not understand why "analogy" should lead us to expect hydrogen chloride to be coloured because chlorine is, or nitric acid to be coloured because NO_2 is; in such cases, we have, I think, at present no reason to expect analogous behaviour, nor indeed any information at our disposal from which conclusions can with justice be drawn.

In the discussion on a previous occasion (*Proc. Chem. Soc.*, 1892, 105), I said that it appeared probable to me that ultimately colour would be traced to that peculiar condition represented conventionally by a double bond, the

atoms being regarded as altogether subordinate. It is perhaps desirable that I should now more fully explain my views as to the manner in which the "quinonoid mechanism" conditions colour.

Briefly, I would suggest that in quinonoid compounds there are two "colour centres," corresponding to and expressed by the symbol $\subset$ in formulæ such as I have used in representing coloured substances. These centres, I imagine co-operate in producing colour through interaction of the light-waves which have traversed them. Substances in which there are no such co-operating centres may absorb generally or selectively in "ultra" and "infra" regions of the spectrum, but without exhibiting "visible colour." In this manner, it is possible, I think, to account for the appearance of colour in substances like diacetyl, $Me \cdot CO \cdot CO \cdot Me$, and dibenzoyl, $Ph \cdot CO \cdot CO \cdot Ph$, in which there are two contiguous $C=O$ groups—*ie.*, which possess a pseudo-orthoquinonoid structure without being quinones.

The colour centres may be likened to elastic gratings, in order to represent the modifications induced by attaching different radicles; in order to account for variation in shade of colour, such elastic gratings may be pictured as undergoing "longitudinal" and "lateral" deformations, varying in extent and character according as the "weight" and character of the attached radicles is varied, and as capable, therefore, of differently affecting the incident rays. However incorrect, from a physical standpoint, this imagery may appear, I trust it will suffice to make my meaning clear.

It is not inconceivable that the distinction which I have sought to make between visible colour and physical colour is no arbitrary one, but is inherent in the human optic mechanism; that our perception of colour, in fact, is itself conditioned by, and exerted through, the agency of quinonoid matters. The discussion of the origin of colour from this point of view, appears, therefore, to be of importance to physiologists, as well as to chemists and physicists.

(To be continued.)

PHYSICAL SOCIETY.

Ordinary Meeting, December 9th, 1892.

Mr. WALTER BAILY, M.A., Vice-President, in the Chair.

Mr. H. E. RAWSON was elected a member of the Society.

The CHAIRMAN announced that an extra meeting would be held on January 13, 1893.

Prof. S. P. THOMPSON's communication on "Japanese Magic Mirrors" was postponed.

Mr. W. B. CROFT, M.A., read a paper on "*The Spectra of Various Orders of Colours in Newton's Scale.*"

After referring to the definition of the order of colours by reference to the retardation wave lengths produced by different thicknesses of selenite between crossed polariser and analyser, the author went on to say that several books on optics implied that the number of bands in the spectra of these colours was the same as the order of the colour. On obtaining selenites of the first four orders of red from Messrs. Steeg and Reuter, he found that the first three orders gave one dark band each, and that of the fourth order three dark bands. Further experiments showed that the thicknesses of the selenites were in the proper proportions required to give the first four orders of red. The numbers of bands, the author explained, depended on the numerical possibilities of wave length within the visible spectrum; that is, whether a multiple of the wave length of one visible wave can be another multiple of a different wave. For example, taking the visible spectrum as extending from A (0.000760 to H (0.000394), and the wave length of the line E in the green as 0.000527, it was shown that the first order of red

was due to extinction of green by a thickness of crystal proportional to 1×0.000527 , and would give one band in the green. For the second order, the thickness of crystal was proportional to 2×0.000527 , viz., 0.001054 , and this number was no other integral multiple of any other wave length between A and H; consequently there could only be one band. Similarly it was shown that the third order of red could only have one band or possibly produce a shortening of the spectrum. With the fourth order of red three bands were obtainable, for—

$$4 \times 0.000527 = 3 \times 0.000703 \text{ and } = 5 \times 0.000422.$$

Three bands were therefore possible near E, A, and G, respectively.

At the conclusion of his paper, Mr. CROFT directed attention to a very simple form of diffraction apparatus, by which most of the ordinary diffraction phenomena could be well seen, and which also served for spectrum observations.

Mr. H. MIERS pointed out that in Lewis Wright's "Practical Optics," a chart showing the bands corresponding to the first four orders of red was given. So far as he was aware, the subject was not fully discussed in the book.

In reply, Mr. CROFT said he had noticed Mr. Wright's chart, but believed that the text implied that the number of bands should be the same as the order of the colour. Tyndall made definite statements to that effect.

Dr. W. E. SUMPNER read a paper on "The Diffusion of Light."

The influence of diffusion in increasing the illumination of rooms and open spaces had not, in the author's opinion, been sufficiently appreciated. Being impressed with the great importance of the subject, he was led to make determinations of the coefficients of reflection, absorption, and transmission of diffusing surfaces. To give precision to terms sometimes vaguely used, several definitions were proposed. *Reflecting power* was defined as the ratio of the amount of light reflected from a surface to the total amount of light incident upon it; *illumination* of a surface, as the amount of incident light per unit of surface; *unit quantity* of light as the flux of radiation across unit area of a sphere of unit radius, at whose centre a unit light is placed; and *brightness* as the candle-power per unit area in the direction normal to the surface. Denoting these quantities by η , I , Q , and B respectively, and assuming the cosine law of diffusion (*i.e.*, the candle-power in any direction is proportional to the cosine of the angle between the direction and the normal to the surface) it was shown that $\pi B = \eta I$, and that the average illumination (I') of the walls of a room is related to the illumination (I) due to the direct action of the lights as expressed by the formula—

$$I' = \frac{I}{1 - \eta}.$$

If the reflecting power of the walls, &c., be 50 per cent, $\eta = \frac{1}{2}$, and $I' = 2I$; whilst if $\eta = 0.8$ (a number approximately true for white surfaces), then $I' = 5I$. The illumination due to the walls may therefore be far more important than that due to the direct rays from the lights. When the surfaces consist of portions of different reflecting power, the average may be found from the equation—

$$\eta = \frac{\eta_1 A_1 + \eta_2 A_2 + \&c.}{A}$$

A being the total surface, and A_1 , A_2 , &c., the areas of surfaces whose reflecting powers are η_1 , η_2 , &c., respectively. This law is shown to be quite accurate for spherical enclosures.

In measuring reflecting power, the surface was attached to a large screen of black velvet placed perpendicular to a 3 metre photometer bench. Two lights were used, one a Methven 2-candle standard placed at the end of the bench remote from the reflecting surface, and the other, a glow lamp of about 20 candle-power, was attached to a

slider which also carried a Lummer-Brodhun photometer. The glow-lamp served to illuminate the reflecting surface, but the photometer was screened from its direct rays. The formulae used in reducing the observations are worked out in the paper, and tables of results given.

Absorbing power was determined by measuring the candle-power of a glow lamp, first when uncovered, and then when surrounded by a cylinder of the substance under test. It was found to be of great importance to distinguish between apparent and real absorption; for reflection from the surfaces of the cylinders increases the internal illumination. The true absorption coefficient (α) is given by—

$$\alpha = (1 - \eta) \frac{k_0 - k_1}{k_0};$$

where η is the reflecting power, and k_1 and k_0 the candle-powers with and without the envelope of material under test.

In determining transmitting power, the Methven standard and photometer were placed on one side of the surface, and the glow lamp on the other. Difficulties were experienced from the fact that some materials, such as tracing-paper, transmit part of the light directly (like transparent substances) and another part by diffusion, according to the cosine law. Methods for discriminating between the different parts were therefore devised, both in the reflection and transmission experiments, and consistent results subsequently obtained. Tables and curves showing the close agreement of calculated and observed values are included in the paper. An abstract of some of the tables of numbers is given below.

Material.	Percentage reflecting power. η .	Percentage absorption. α .	Percentage transmission. τ .	$\eta + \alpha + \tau$.
Blotting paper ..	82	13.8	9.2	105.0
Cartridge paper ..	80	12.2	11.2	103.2
Tracing cloth ..	35	15.0	54.4	104.4
Tracing paper ..	22	7.0	76.0	105.0
Ordinary mirror ..	82	—	—	—
Ordinary foolscap	50 to 70	—	—	—
Tissue paper (one thickness) ..	40	—	—	—
Tissue paper (two thicknesses) ..	55	—	—	—
Yellow wall paper	40	—	—	—
Blue paper ..	25	—	—	—
Dark brown paper	13	—	—	—
Yellow painted wall	20	—	—	—
Black cloth ..	12	—	—	—
Black velvet ..	0.4	—	—	—
Arc lamp globes—	—	Apparent	—	—
Light opal ..	—	15	—	—
Dense opal ..	—	39	—	—
Ground glass ..	—	42	—	—

Theoretically, the sum of the reflecting, absorbing, and transmitting powers should be unity, but from the above Table it will be noticed that they exceed one-hundred per cent by amounts greater than can be accounted for by experimental error. This discrepancy the author thought might be attributed to the law of cosines not being exactly fulfilled.

Mr. A. P. TROTTER said he had been interested in the subject of diffusion for many years with a view to obviating the glare of arc lamps. Some experiments he made on reflecting power gave unsatisfactory results, owing, as he now saw, to his not taking the solid angles subtended by the reflecting surfaces into account. The reflecting power of substances was of great importance in the illumination of rooms; in one case, measured by Dr. Sumpner and himself, two-thirds of the total illumination was due to the walls. It would greatly simplify measurement of reflecting power if some substance could be adopted as a standard.

Referring to the cosine law, he said he had found it true, except when the angles of incidence approached 90° . In cases where considerable total reflection took place, the apparent brightness near the normal direction was greatly in excess of that in other directions. These points he illustrated by polar curves. He had also considered what should be the nature of a roughened or grooved surface to give the cosine law of diffusion. No simple geometrical form of corrugations, &c., seemed to fulfil the required conditions.

Dr. HOFFERT said the high numbers given for the reflecting powers of substances were very interesting. Most people had noticed the effect of laying a white tablecloth in an ordinary room. He had also observed that wall papers of the same pattern, but slightly different in colour, had very different effects in producing increased illumination, and wished to know if the influence of small differences in colour and texture on diffusing power had been investigated.

Mr. BLAKESLEY defended the cosine law and suggested that the summation of the powers exceeding unity might be due to the fact that the enclosure reflected heat as well as light, thus raising the temperature and increasing the efficiency of the radiant.

Mr. ADDENBROOKE said the importance of the subject was impressed on him when he passed through America three years ago and noticed the crude manner in which electric lighting was there carried out. If using good reflecting surfaces increased the illumination of a room 50 per cent, it was like reducing the cost of electricity from 8° to 4° per unit. He could hardly conceive any subject of more practical importance than the one before the meeting.

Dr. C. V. BURTON did not understand why the cosine law should be objected to, for it was possible that no surface was perfectly diffusive. The effect of reflection from walls, &c., say in illuminating a book, would not, he thought, be so great as would appear from the numbers given, for one usually read near a light, and the reflected light falling on the book was only a small part of the whole, on account of the greater distances of the walls.

Another MEMBER pointed out that in experiments such as those described, it was very important to screen the photometer and surfaces from all radiation other than that under test. He rather doubted whether any surface reflected as well as mirrors. White surfaces might appear to do so, but this was probably because the eye would over-estimate it, owing to the superiority of white in aiding distinct vision.

Dr. SUMPNER, in reply, said he had, as stated in the paper, used white blotting-paper as a standard of reflecting power, and found it very convenient. His most careful measurements had been made on whitish surfaces, and not on coloured ones. Where one colour, say red, preponderates in a room, the average light would be much redder than that emitted by the source owing to the other colours being absorbed.

In considering illumination as related to distinct vision, it was necessary to take account of the eye itself, for the pupil contracted in strong lights and opened in feeble ones. This subject he hoped to treat fully in a subsequent paper.

Action of the Chlorides of Bibasic Acids upon Sodium Cyanacetic Ether.—Th. Müller.—In the action of succinyl chloride upon sodium cyanacetic ether there are formed two products, which may be separated by means of sodium carbonate, succinocyanacetic ether, insoluble in this reagent, and succinodicyanacetic ether, which dissolves in it with escape of carbonic acid. The author does not decide on the constitution of these two ethers, though the former has probably a dissymmetric constitution. The other is doubtless a symmetric compound.—*Comptes Rendus*, cxv., No. 22.

NOTICES OF BOOKS.

Berzelius and Liebig. Their Correspondence from 1831 to 1845; with Explanatory Additions from the simultaneous Correspondence of Liebig and Wöhler, as well as Scientific References. ("Berzelius und Liebig. Ihre Briefe von 1831 bis 1845; mit erläuternden Einschaltungen aus gleichzeitigen Briefen von Liebig und Wöhler so wie, wissenschaftlichen Nachweisen herausgegeben, mit Unterstützung der kgl. Bayer Akademie der Wissenschaften von JUSTUS CARRIÈRE.") Edited by JUSTUS CARRIÈRE, with the Assistance of the Bavarian Academy of Sciences. Munich and Leipzig: J. F. Lehmann.

THIS collection of letters is a most precious document for all who feel an interest in the history of chemistry during the second quarter of the present century, and in the life and character of some of its most distinguished representatives. Berzelius and Liebig appear here doubtless as genuine men of science, actuated by a pure disinterested love for truth, but at the same time as somewhat prone to take offence and sufficiently severe towards opponents. Wöhler, on the contrary, equally devoted to science, displays here his genial, kindly disposition in seeking to smooth over offences and to explain misunderstandings. Not a few of their contemporary *savants*, French and English, as well as German, experience warm denunciations. Whether Berzelius or Liebig is the more outspoken on such occasions would be hard to decide. Liebig defends his old master, Gay-Lussac, against the mistaken dislike expressed by Berzelius; but he admits that a certain mental indolence restrains the French, to their disgrace, from making themselves acquainted with foreign research. Gay-Lussac, he adds, fears that this tendency will lead to the extinction of all scientific feeling in France.

Dumas is humorously spoken of as a Jesuit, named Ignatius, and accused of "impudent falsehoods." The scientific men, alike of Paris and Berlin, are pronounced "jealous *savants* who never enjoy science, but merely their momentary reputation."

We find a notice of the controversy touching the discovery of vanadium. Humboldt claimed the honour for Del Rio, whilst Berzelius insists upon the rights of Sefström. Possibly the position of Del Rio would have been stronger if he had not yielded to the influence of Descotils, who insisted that it must be chrome.

Under date May, 1831, Liebig characterises Giessen as a place where the dreariest pedantry has set up its throne, and where the natural sciences were taught only out of Greek authors, or from the writings of Wilbrand. So that in spite of the influence of Oken, the avatar of natural science in the German universities is still a thing of yesterday.

In 1832, Liebig admits that he has forfeited all hopes of being elected a correspondent of the Institute by publishing his opinion on the character of French chemists and on the decay of chemistry in France.

In 1833 we find Liebig denouncing the calumnies of Löwig, who had written against him a pamphlet in which the dates and the connection of certain letters were falsified. "I was," says Liebig, "for the first moment petrifed at his impudence in falsehood."

In the next following letter, Berzelius is scarcely less exasperated at Brand, who has written: "Everything intelligible in Berzelius's writings is borrowed from Sir Humphry Davy." This strange and baseless assertion would be the more unwelcome to Berzelius, since it is an open secret that he had formed no favourable opinion of Davy.

Berzelius, in 1834, expresses himself on the subject of nomenclature. He holds that names should have not more than one syllable, or, at most, two syllables. "How many bad names have we not obtained by plundering the

Greek lexicon!" What would Berzelius have said had he survived to our times?

Liebig compares Mitscherlich to a leech, which sucks the blood of all it encounters and then flings them away.

In 1837 we have remarks on the contest between Pelouze and Pelletier for a vacant seat in the Academy. Both Berzelius and Liebig give their good wishes to Pelouze, whom Dumas opposes from envy, and d'Arcet from revenge. In the same year, Liebig, by occasion of a visit to England, where he says that he has "seen much, and learnt little. England is not the land of science, but of an exaggerated dilettantism. The chemists are ashamed of being called chemists because the "apotheker," who are not respected, have appropriated the name."

The chemists now, if we are to accept a decision of "Tom Brown," have no legal right to be called chemists, which is, it seems, the exclusive property of the vendors of medicines and the compounders of prescriptions. Would that they could be prevailed upon to call themselves pharmacists or pharmacutists.

Liebig, however, admits that Graham is, in a scientific point of view, a most valuable exception.

We find that in the following winter Liebig was elected a member of the Swedish Academy of Sciences. His competitors were Faraday, who obtained one vote, and Dumas, who obtained none at all! In the same season he was reconciled with Dumas, at least in appearance.

In February, 1838, Berzelius advises Liebig to cease being the "chemical executioner," and tells him that he stands so high that he does not need to tread others down.

In the succeeding letter we learn that at Mitscherlich's instigation a Ministerial decree forbade Prussian subjects to study chemistry or pharmacy at Giessen!

If we follow these letters to the end, we shall see that a coolness between Liebig and Berzelius gradually made its appearance, and in spite of the effort of Wöhler, could no longer be removed. Berzelius died in his 69th year, and Liebig in his 70th. Berzelius had gone so far as to warn students not to make themselves the instruments of Liebig.

Both these illustrious men would have regarded each other and their contemporaries with different eyes had they enjoyed good health.

Aids to Chemical Science. For Teachers and Students; more especially for those Preparing for Class "D" Examination of the New Zealand Education Department. By ANDREW GREY.

THE author dates his preface from Remuera, Auckland. The book is printed by Spottiswoode and Co., but we do not find any publisher's name, though there is a list of agents in different cities of New Zealand.

The experiments, which are well selected, illustrate the fundamental ideas of matter and energy, the conditions of matter, gravitation, mechanical powers, sound, light, heat, magnetism, electricity, chemistry, physiology, and health.

The least satisfactory portion of the book comprises the "examination papers." It is strange and sad that in our colonies the examination system of education is adhered to with a faith truly touching.

Catechism Series.—Chemistry. Part I.: Inorganic. Chemistry. Part II.: Inorganic and Organic. No Author's name. Edinburgh: E. and S. Livingstone.

PROBABLY not a few of our readers are acquainted with Hood's unfinished novel "Catechism Jack;" the hero of which is a somewhat dull youth who has been so thoroughly drilled in the Church Catechism that it supplies him with an answer to every possible question. We

were of opinion, however, that in Science, at least, this way of administering instruction had vanished with Pinnock. We hoped that teachers of all grades had become aware that the catechised student falls into the habit of correlating his knowledge with certain questions or even certain forms of questions, and consequently feels bewildered if taken out of his usual routine. Such books as those before us are undoubtedly well adapted to the examination system, which is an unfortunate feature. It is truly painful to look over the list of publications here subjoined, and to note how many are actually praised on this account.

We fear that examinationism, like other noxious aliens, will prove fearfully hard to banish. We can see to what a state of stagnation it has reduced its native country, China, but we close our eyes.

Would it be too much to request every author who feels tempted to write an examinational text-book to read over and digest the protest of Mr. Auberon Herbert and his friends.

Book of Chemical Labels for use in connection with Science and Art Classes. Price Ninepence.—*Book of Chemical Labels for use in the Laboratory.* Price One Shilling. Compiled by PHILIP HARRIS and Co., 144 and 146, Edmund Street, Birmingham.

Good labels are a very necessary adjunct to a laboratory, and these two books present all the most used labels in a convenient form. The type is clear, the paper good and not too thick, the gum at the back sticks well to glass, and the plan of half cutting through the paper in a continuous line enables the labels to be torn off without leaving an unsightly edge, as is the case when perforations in the postage stamp fashion are used. Plenty of duplicates of the more commonly occurring chemicals are given. "Oxalic Acid," of which there is only one solitary example in the two books, being a striking exception. Partly printed labels to be filled up in ink, according to laboratory requirements, are to be found; and a full list of standard solutions, together with several blank labels, are met with at the end of each book.

Arithmetical Chemistry. Part II. By C. J. WOODWARD, B.Sc. New Edition. London: Simpkin, Marshall, Hamilton, Kent, and Co. Birmingham: Cornish Bros.

THIS new edition is a great improvement on the previous one. The book has been entirely re-written and many additions have been made; it consists essentially of lessons on the various branches of chemistry and chemical physics, each lesson followed by a number of questions on the particular subject just explained: these should be found very useful in schools and colleges. A good index is provided, as well as a convenient table of logarithms taken from the "A B C Five-Figure Logarithms," by the same author.

Gems and Precious Stones of North America. By G. F. KUNZ. Appendix I. and II.

THE author mentions here several instances of diamonds having been found in Wisconsin and Georgia, as also in a meteorite which fell at Cañon Diablo, Arizona. These stones are of little commercial value, but they are important as bearing upon theories of the origin of the diamond. The chief deposits of this stone have hitherto been peculiar to the Southern hemisphere, or at least the equatorial region. Hence it has been surmised that they may have fallen from a flight of meteorites which crossed the more southern regions of our globe. The North American specimens, like those found in Russia, do not bear out this conjecture, though they are perfectly in harmony with the supposition of the meteoritic origin of the diamond.

Sapphires appear to have been found in Montana in the estimated quantity of 2000 ozs. per acre; but their colour is neither a true red (ruby) nor a true blue, whence they are in little request.

Turquoise is abundant in Grant County, New Mexico, and seems to have been mined for by the aborigines.

The treatise is a valuable contribution to the geographical phase of mineralogy, a science which is now very eagerly cultivated in the United States.

CORRESPONDENCE.

THE POSITION OF CHEMISTS.

To the Editor of the Chemical News.

SIR,—The time certainly is now that an understanding should be arrived at amongst chemists by which they may be enabled to receive for their indispensable services that consideration which the dignity of their calling demands.

Such is the condition of affairs at the present moment that, although good chemists are absolutely necessary in all classes of chemical works and establishments, it is unfortunately a fact that their services are generally considered of less importance than that of the cashier or principal clerk in the office. This is made manifest by the salary offered and paid to the chemist.

An examination of the columns of such papers as are devoted to the profession will show the absurdly low salaries for which chemists are expected to devote their services and energies to their employers. Why is this? Is it because the chemical profession is undergoing retrogression? or is it because of the number of pseudo-chemists who are anxious at any price to enter into and serve an apprenticeship to practical technical work? When such a salary as £80 per annum is offered by a large corporation for a gas-works' chemist, it certainly proves that his commercial value is far and away below par.

Now, what is the reason of such a condition of things? One is prompted to think seriously that it is the result of the actions of chemists themselves; for so long as employers are able to obtain cheap labour they will continue so to do. So long as a chemist will sell himself for such a salary as an ordinary mechanic would scorn, so long will the march of the chemical profession be one of degradation.

When the Institute of Chemistry was established it was fondly hoped that it would be the means of raising to a nobly high standard those who have taken a chemical calling as a means of livelihood. But the Institute does not appear to have grasped the absolute soul of the case, and there are no doubt many men who have obtained the right to the use of the letters F.I.C., and even far higher attainments, at the present time selling the results of their hard study and long, expensive training for such a sum as £2 per week!

A remedy by which a much desired change may be brought about must be a matter to be settled amongst chemists themselves, and when once begun must not be permitted to receive a single check, but proceed steadily onwards and upwards until the goal is reached.

As a suggestion, we may form first of all a home combination, and when this is on a solid foundation invite our foreign brethren to associate themselves with us, and thus make a solid International combination. There are very few employers of chemical talent who would do otherwise than give us their utmost support.

It is not proposed to propound any set scheme in this letter, but feeling sure that chemists generally will seriously consider what they think should be done, it is left for them to criticise and formulate suggestions upon which a definite scheme may be founded.

The writer will be pleased to receive any communica-

tions on the matter, and will form one cog in the wheel which it is hoped will carry us safely and surely into a more fortunate condition of things which we honourably and rightfully claim.

If this idea is well ventilated, and if other chemists will give expression to their views in these columns, this, together with an interchange of ideas at meetings held at certain centres, would no doubt promote steady and solid progress.—I am, &c.,

T. H. DAVIS.

DISINFECTANTS—AN EXPLANATION.

To the Editor of the Chemical News.

SIR,—Will you grant me space, in order to avoid misunderstanding, to make the following explanation:—

1. I recently learned that certain samples marked "Aminol, a true disinfectant" have been sent to various gentlemen accompanied by a leaflet, in which my name, without my authority, is associated with these samples. Allow me to inform your readers that these samples contain "aminol" in water in the strength of one in five thousand. Now, the experiments which I carried out with "aminol" as regards its disinfecting power on microbes, were made with a solution of the strength of one in six hundred, and the disinfecting power of this strength was the following:—Spores of anthrax bacilli remained unaffected after eight hours' exposure; only after an exposure for twenty-four hours did the number of living spores decrease, but some escaped disinfection even after so long an exposure. Anthrax bacilli, *Staphylococcus aureus*, and others were destroyed, but only after a prolonged exposure.

2. A substance is advertised and circulated under the name of "periodate crystals," and is associated with my name without my authority. Until quite recently I have made no experiments with it. A few years ago I made a few experiments, merely of a tentative character, with a solution which was labelled "periodate," but not with the substance advertised as "periodate crystals." With these latter I have recently made experiments, and I find that their solution in full strength has no disinfecting power on microbes, pathogenic and non-pathogenic, amongst which may be mentioned the bacillus and spores of anthrax, the bacillus of typhoid and of diphtheria, of cholera and of erysipelas, the *Bacillus prodigiosus*, the *Staphylococcus aureus*, and others. Likewise I find that injection of large quantities of the solution into guinea-pigs already infected with anthrax or diphtheria has no power whatever in arresting or altering the normal course of these diseases to their fatal issue.—I am, &c.,

E. KLEIN.

ORIGIN OF THE VARIOUS COLOURS OF NITRIC ACID.

To the Editor of the Chemical News.

SIR,—My attention has been called to an article by Dr. Marchlewski upon the above subject in the *CHEMICAL NEWS*, vol. lxvi., p. 271. The writer feels himself "driven to conclude" (1) that I have only read his first communication (*Ber.*, xxiv., 3271) hurriedly, (2) that I have not read his second communication (*Zeit. Anorgan. Chemie*, i., 380) at all, and (3) that I suggest the carrying out of useless experiments.

Firstly, I can merely express my regret that I should have appeared to have read without due care the first paper by Dr. Marchlewski. Secondly, if he will kindly refer to my paper "On the Conditions of the Formation and Decomposition of Nitrous Acid" as it appears in the *Proc. Roy. Soc.*, vol. lii., p. 27, he will find that it bears the superscription "Received April 12, 1892." Dr. Marchlewski's second paper in the *Zeit. Anor. Chemie* bears

the date June 24, 1892. When my paper was sent to the Royal Society I had not read Dr. Marchlewski's second paper, for the obvious reason that it had not appeared. Thirdly, I am quite unaware that I have suggested either to Dr. Marchlewski or any other person any experiments, useless or otherwise, upon the subject.

Lastly, if in any future paper I shall have occasion to allude to Dr. Marchlewski's work, he may rest assured that I shall do so not only without criticism but without comment, as I would wish to avoid the risk of being misinterpreted and misunderstood.—I am, &c.,

V. H. VELRY.

The University Museum, Oxford.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 22, November 28, 1892.

The Existence of Distinct Nerve-Centres for the Perception of the Fundamental Colours of the Spectrum.—A. Chauseau.—The author concludes that: 1. Green, by direct demonstration, and red and violet by deduction, seem entitled, physiologically speaking, to the character of fundamental colours which has been ascribed to them by Young. 2. There are, in fact, in the nerve-centres distinct cellules for the perception of these colours, and at least endowed with three independent sensibilities—one which is excited by the vibrations of the red, another by those of the green, and a third by the vibrations of the violet. 3. These properties obscured during sleep do not resume their activity simultaneously. The aptitude for the perception of green is the first to wake up. 4. A man who has fallen asleep near a window which allows the light of the sky to fall almost equally upon both his eyes, sees, on raising his eyelids in the moment of awaking, all white or grey objects in the room momentarily illuminated with a very bright pure green. 5. The normal eye has therefore the power of analysing white light, and decomposing it into its fundamental colours. (If we have been for some time in a dark mine or cavern we see on extinguishing the tapers and stepping out into the open air all external objects illuminated with a beautifully pure green which disappears in a moment).

The Fusion of Calcium Carbonate.—A. Joannis.—The author in his experiments has kept chalk for a quarter of an hour at a temperature above the melting-point of gold. The pressure of the gases was maintained constant at about fifteen atmospheres. In two experiments in which the iron tube resisted to the end, the chalk was converted into a material comparable to marble in hardness, presenting a distinctly saccharoid fracture, but with a grain finer than that of marble. Fragments of this material are translucent along the edges. It admitted of being polished and reduced to thin laminae.

Action of Antimony upon Hydrochloric Acid.—A. Ditte and R. Metzner.—Hydrochloric acid has no action upon antimony. Hydrogen is never evolved when the two substances are brought in contact, and any antimony dissolved is due merely to the intervention of oxygen, the quantity being proportional to the weight of this gas contained in the liquids.

The Alkaline-Earthy Zincates.—G. Bertrand.—The author describes the calcium, strontium, and barium zincates. The calcium salt is easily obtained by adding a saturated solution of zinc oxide to a large volume of lime water. The flocculent precipitate of calcium zincate first formed is at once re-dissolved in a large excess of ammonia, and the mixture is left under a bell-glass in

presence of sulphuric acid. The zincate is gradually deposited in crystals. The mother-liquor is decanted off, the crystals are rapidly washed in boiled distilled water and dried *in vacuo*. Their composition answers to the formula $Zn_2CaH_2O_{24}H_2O$. The strontium and barium compounds cannot be obtained in a similar manner. The author dissolves 150 grms. strontium hydroxide in 1.5 litres hot water, adding a solution of 100 grms. zinc sulphate in 500 c.c. of ammonia (containing 10 per cent NH_3). After settling for twenty-four hours the strontium sulphate is filtered off, and the clear liquid saturated with strontia is placed under a bell in presence of sulphuric acid. A fall of temperature diminishes the solubility of the strontia, which crystallises simultaneously with zinc hydroxide and strontium zincate. The three kinds of crystals can easily be separated with forceps. The barium compound is obtained in a similar manner.

The Anhydrous and Crystalline Iron Fluorides.—C. Poulenc.—The author communicates three methods for the preparation of these compounds:—(1) The action of hydrofluoric acid upon the metals at a high temperature; (2) the action of hydrofluoric acid upon the chlorides and the oxides; (3) transformation of hydrated into anhydrous fluorides by the action of hydrofluoric acid.

Preparation of Metallic Chrome by Electrolysis.—Em. Placet.—The author electrolyses an aqueous solution of chrome-alum, to which an alkaline sulphate and a small quantity of sulphuric acid have been added. The metal is very hard and has a fine bluish white colour. It is not affected by the atmosphere and is not attacked by concentrated sulphuric acid, nitric acid, or potassa. A specimen weighing more than 1 kilo. was exhibited to the Academy.

The Preparation of Hydrobromic Acid.—E. Léger.—This paper will be inserted in full when practicable.

Reply to the Observations of M. Friedel on the Rotatory Power of the Salts of Diamines.—Albert Colson.—For this controversy we must refer to the original.

The Melting-Points of Solvents as the Lower Limit of Solubilities.—A. Etard.—This paper requires the accompanying diagrams and tables.

Researches on the Colours of Certain Insects.—Dr. A. B. Griffiths.—The wings of Lepidoptera and of other insects contain a certain number of colouring-matters. Only one true pigment has hitherto been studied, the yellow principle of the wings of some Lepidoptera (see J. G. Hopkins, *Proc. Chem. Soc. of London*, 1889, p. 117). The author has determined the composition of the green pigment in the wings of the following Lepidoptera:—*Rhopalocera*—*Papilio* (several species), *Parthenos gambrisius*, *Hesperia*, *Limenitis pocris*, *Noctua*—*Halius prasinana*, *Geometra*—*Larentia* (several species), *Cidaria miata*, *Sphingida*—*Ino statites*. The same pigment is always yielded by each of these species. The wings were first treated with hot alcohol and ether, in which liquids the pigment is insoluble. The wings were then boiled in acidulated water and the filtrate was concentrated by evaporation. The green pigment deposited as an amorphous substance. The operation was repeated several times. The mean of six analyses of this green pigment gave results answering to the formula $C_{11}H_{12}N_2O_{10}$. The pigment is a bibasic acid, soluble in acids and precipitable by silver nitrate. The mean of three analyses of the silver salt leads to the formula $C_{11}H_{10}Ag_2N_2O_{10}$. The silver salt appears in silky, colourless needles very soluble in alcohol, but insoluble in ether. The alcoholic solution deflects the plane of polarisation to the right. Its specific rotatory power for the ray D is $[\alpha]_D = +29^\circ$. By prolonged boiling with water the acid pigment gives urea, alloxane, and carbonic acid. By the prolonged action of boiling hydrochloric acid the pigment is converted into uric acid. It is very probable that the green pigment is a derivative

of uric acid, and that it is deposited in the wings by the wandering cellulose, *i.e.*, it is of an excretory character. The author gives it the provisional name of lepidopterac acid. (It is to be regretted that Dr. Griffiths has not examined the absorption spectrum, if any, of this pigment).

Microbicide Action of Carbonic Acid.—Cl. Noury and C. Michel.—Milk saturated with CO_2 under pressure and kept in the cold coagulates only after the lapse of eight days, whilst ordinary milk curdles in general in forty-eight hours at the utmost. The same milk raised to the temperatures of 45° , 65° , and 80° , coagulates under the ordinary conditions. If heated to 120° it curdles at once. Carbonic acid retards the action of microbia, but it does not seem to be a true microbicide.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements before Easter:—Sir Robert Stawell Ball, six lectures (adapted to a Juvenile Auditor) on "Astronomy"; Professor Victor Horsley, ten lectures on "The Brain"; the Rev. Canon Ainger, three lectures on "Tennyson"; Professor Patrick Geddes, four lectures on "The Factors of Organic Evolution"; the Rev. Augustus Jessopp, three lectures on "The Great Revival—a Study in Mediæval History"; Professor C. Hubert H. Parry, four lectures on "Expression and Design in Music" (with Musical Illustrations); the Right Hon. Lord Rayleigh, six lectures on "Sound and Vibrations." The Friday Evening Meetings will begin on January 20th, when a discourse will be given by Professor Dewar on "Liquid Atmospheric Air"; succeeding discourses will probably be given by Mr. Francis Galton, Mr. Alexander Siemens, Professor Charles Stewart, Professor A. H. Church, Mr. Edward Hopkinson, Mr. George Simonds, Sir Herbert Maxwell, Bart., the Right Hon. Lord Rayleigh, and other gentlemen.

The Photography of the Light Waves of the Smallest Wave-Lengths.—At the Meeting of the Mathematical and Natural Science Section of the Imperial Academy of Sciences of Vienna, on November 10th, Prof. V. von Lange presented the following communication from the engineer Vidor Schumann, of Leipzig, a copy of which he has courteously forwarded us:—The photographic energy of the ultra-violet rays on collodion and gelatin plates decreases strikingly at the wave-length $200\ \mu$, and falls off to a similar extent towards the more refrangible side. The cause of this decline in energy lies in the fact which I have established spectrographically; (1) in the impermeability to light of the collodion and gelatin, in which the sensitive ingredient of the coating of the plate, *i.e.*, the silver haloid, is embedded, and (2) in the impermeability of the air which the rays have to traverse on their way to the plate. If we remove these two absorbents the silver haloid shows itself many times more sensitive for the rays beyond $200\ \mu$ than it was in presence of the collodion and gelatin, and the photographic efficacy extends far beyond the previous limit of the ultra-violet light (wave-length $185\cdot2\ \mu$). The production of a film of pure silver haloid on the plate offers great difficulties. A method for this purpose was hitherto not known. After numerous experiments I found a process by which I have now for two years prepared all the plates which I have required for observing the rays beyond the wave-length $185\cdot2\ \mu$. The air could only be removed from the rays by exhausting the spectrograph. In this manner I have hitherto been able to follow about twenty different spectra far beyond $185\cdot2\ \mu$. All of them develop here an unexpected wealth of rays, but none to so high a degree as the hydrogen light of the Geissler tube. I estimate the number of the hydrogen lines, which I have isolated at 600, and the shortest of their wave-lengths at

$100\ \mu$. I have not as yet effected the measurements, for which, however, I have already made preparations. For illustration the speaker exhibited a tableau composed of H. V. Schumann's original plates, showing the portion of the ultra-violet hydrogen spectrum first photographed by the latter.

MEETINGS FOR THE WEEK.

TUESDAY, 20th.—Institute of Civil Engineers, 8.
Pathological, 8.30.
WEDNESDAY, 21st.—Meteorological, 7.
Geological, 8.
Microscopical, 8.

TO CORRESPONDENTS.

Muriate of Ammonia.—A German firm wishes to know the names of English firms who manufacture this article in large quantities.

ERRATUM.—P. 253, col. 1, line 33 from top, for "halium" read "potash alum."

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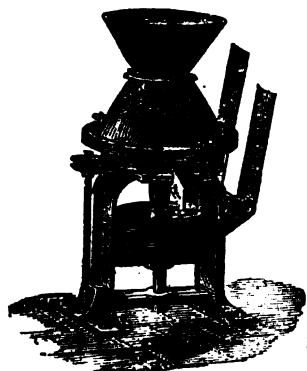
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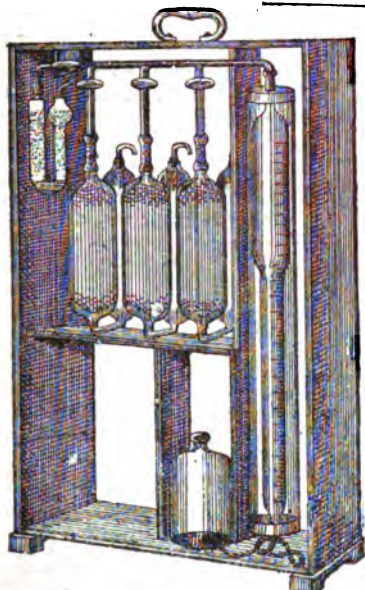
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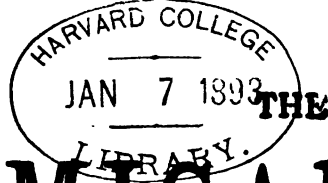
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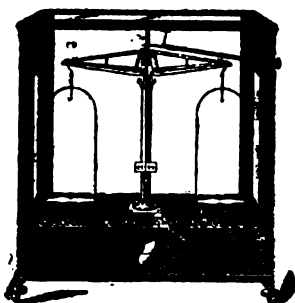
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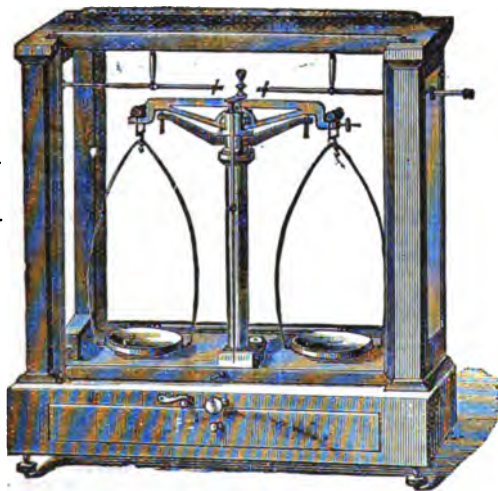


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THE CHEMICAL NEWS.

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STUDIES ON THE EARTHS OF THE CERIUM AND YTTRIUM GROUP.*

By A. BETTENDORFF.

On the Earth *Ya* or *Gadolinita*.

In the year 1878 Lawrence Smith drew the attention of chemists to the occurrence of new cerite and ytterite earths in the Samarskite of North Carolina. He extracted from them an oxide of a deep orange-yellow colour, the equivalent of which $RO=109.0$. The solutions of its salts displayed no absorption-bands. He did not sufficiently characterise this earth, the radicle of which he named *mosandrum*. Marignac and Delafontaine considered it as identical with *terbia*, the existence of which had become questionable in consequence of the researches of J. Bahr and R. Bunsen, as also of P. T. Cleve and O. M. Höglund, but was persistently upheld by Delafontaine.

An investigation of the earths of samarskite executed by this chemist showed in fact the presence of *terbia* as well as of other new earths, but he also did not succeed in their separation and distinct characterisation.

In 1880 Marignac examined the oxides of Samarskite, and obtained along with samaria ($Y\delta$) an earth of an orange-yellow colour, the colourless saline solutions of which showed no absorption-bands, and the equivalent of which $RO=120.5$. It was distinguished from yttria by the slight solubility of its formate and of its double potassium sulphate, and it could not be mistaken for ytterbia on account of the greater permanence of its nitrate when heated. As Marignac considered it possible that this earth might be identical with that discovered by Delafontaine he named it provisionally *Ya*.

In 1886 W. Crookes announced that by fractionated precipitation of the earths of Samarskite with a dilute solution of ammonia, he had separated from the mean fractions an oxide showing all the properties of the earth *Ya*, and distinguished by a peculiar light-spectrum. He obtained subsequently the same spectrum from a specimen of *Ya* given him by Marignac, and ascertained that Lawrence Smith's oxide *mosandra* was a mixture of yttria with other earths, and possessed none of the properties of *Ya*. As Lecoq de Boisbaudran almost simultaneously recognised a specimen of the earth prepared by Lawrence Smith as a mixture, and as Delafontaine's supposed new earths were not confirmed, Marignac gave to the earth *Ya* the name *gadolinia*, with the symbol *Gd* for its radicle.

Lecoq de Boisbaudran then, with material supplied him by Marignac, effected careful determinations of equivalents, and described the spark-spectrum of gadolinium chloride. Some results of the researches of P. T. Cleve on gadolinia were made known by the publications of Lecoq de Boisbaudran.

Gadolinia is contained in considerable quantity in the orthites of Strömboö, near Arendal, as also of Hitterö, which have furnished me the material for experiments on the cerite and ytterite earths. In a former communication I announced the method of separating samaria from *terbia* and gadolinia, and that there was obtained a mixture of the latter of a reddish-yellow colour contaminated merely with small quantities of samaria.

The concentrated solution of *terbium* and gadolinium nitrates, if mixed with a saturated solution of potassium sulphate, and if allowed to stand quietly, gives no pre-

cipitate of the double salts even after the lapse of many days. Precipitation occurs on violent and prolonged shaking, and is completed after a considerable time. But the earths which have remained in solution as a double salt differ but little in their equivalents, so that a separation cannot be effected in this manner. By means of a fractionated precipitation of the nitrates with dilute ammonia precipitates were at once obtained containing oxides of higher equivalent $RO=120.15$ to 120.40 , and were distinguished by a deeper colour. After a series of systematic precipitations there was finally obtained a feebly basic earth, $RO=122.0$, of a dark brown colour, consisting chiefly of *terbia*. On the other side there was obtained a more strongly basic oxide of a very faint yellowish colour, $RO=119.68$, containing especially gadolinia.

On a spectroscopic examination of these two earths the concentrated solutions of the nitrates showed that all traces of samaria, still contained in the final product $RO=119.96$, had accumulated in the gadolinia material, whilst the *terbia* material was perfectly free. For the further purification of the gadolinia, the solution of the nitrate was again submitted to a series of fractional precipitations with dilute ammonia, and the observation of Lecoq de Boisbaudran was confirmed that the samaria passes over in the first precipitations, and is therefore with relation to ammonia more feebly basic than gadolinia. The samaria was now systematically introduced into the first precipitates, and these were freed from it by treating their concentrated neutral nitrate with potassium sulphate in the manner laid down (*Annalen*, cclxiii., 165). These first purified fractions of gadolinia had an equivalent of $RO=119.90$, whilst the fractions last precipitated with ammonia were $RO=120.09$ to 120.16 . A spectroscopic examination showed that the latter contained mere indications of the absorption-lines of samaria, which came up rather more strongly in the fractions $RO=119.90$.

In order to obtain a gadolinia as free as possible from samaria, the following method was taken. All the fractions $RO=119.90$ to 120.16 , amounting to 12.3 grms., were united and dissolved in the necessary quantity of nitric acid. The solution, evaporated to a syrup on the water-bath, congealed on cooling and stirring to a colourless crystalline powder, whilst the excess of nitric acid escaped as a vapour. The saline mass was still heated for some time upon the water bath, and thus the neutral nitrate was ultimately obtained. It was dissolved in a little water and put in a 1 litre bottle containing 600 c.c. of a saturated solution of potassium sulphate and a considerable quantity of the same salt in the state of a fine powder. The whole was allowed to stand for three days with frequent violent agitation, and the solution was filtered off from the double salt which had been formed and from the undissolved excess of potassium sulphate. The volume of the filtrate was measured, the earth separated from it was weighed, and its equivalent was determined. The earth separated from the precipitated double salt was also separated, and with it the same procedure was repeated. Thus two constants served as a measure for the unity and purity of the earth, i.e., its equivalent, and the proportion of solubility in a saturated solution of potassium sulphate, which latter value must be constant for a unitary salt at one and the same temperature.

Fraction I.—1.0682 grms. gadolinia yielded 1.7779 grms. gadolinium sulphate, $RO=120.20$, $R_2O_3=360.60$.

Fraction II.—1.0580 grms. gadolinia yielded 1.7611 grms. gadolinium sulphate, $RO=120.17$, $R_2O_3=360.51$.

Fraction III.—1.0796 grms. gadolinia yielded 1.7969 grms. gadolinium sulphate, $RO=120.19$, $R_2O_3=360.57$.

(To be continued.)

Fusion of Calcium Carbonate.—H. Le Chatelier.—The author, unlike M. Joannis, finds that the fusion and crystallisation of precipitated calcium carbonate may be produced by heat alone without the intervention of an elevated pressure.—*Comptes Rendus*, cxv., No. 23.

* From *Liebig's Annalen*.

THE ABSORPTION OF ATMOSPHERIC NITROGEN BY VEGETATION.

As the long discussion concerning the source of the nitrogenous matter of plants seems to be drawing to a close, it may be useful to summarise the successive stages of the dispute, and to show the conclusion towards which Science and practice are jointly tending.

In 1849 it was generally admitted,—to no small degree on the faith of the experiments of M. Boussingault,—that plants derived their nitrogen either from nitrogenous manures or from the ammonia present in the atmosphere. In the same year M. Georges Ville, experimenting upon lupins and cress, found that whilst the plants had absorbed 103 m.grms. of nitrogen, the air had scarcely introduced 1 m.grm. of nitrogen into his apparatus in the form of ammonia.

Entering upon a very extended series of determinations of the ammonia in the air, he arrived at the conclusion that it contains on the average 23.11 grms. of ammonia per million kilos. Twenty-six years later M. Schloesing undertook the same determination, but instead of one million kilos. he took as his unit 100 cubic metres, in which he found 2.56 m.grms. of ammonia. Hence no comparison of his results with those of M. Ville was possible without a previous calculation. But on reducing both these results to the same standard (100 cubic metres of air), it appears that the difference between the two determinations is trifling. We have according to—

G. Ville	2.84 m.grms.
Schloesing	2.56 ..
Difference.. ..	0.28 ..

The difference, therefore, in 130 kilos. of air is merely 2-10ths of 1 m.grm. M. Schloesing, however, still assumes the attitude of the first and true determiner of the quantity of ammonia in the air.

As far back as 1849 M. Ville also established the fact that atmospheric nitrogen is absorbed by cress. This fact has been indeed denied, but it has been fully confirmed by M. Bréal (*Annales Agronomiques*, xviii., p. 269) and M. P. P. Dehérain. MM. Schloesing, jun., and Laurent have since shown that certain of the lower plants are capable of fixing free nitrogen, and Professor Berthelot has proved the same fact as occurring during the growth of the amaranths. Hence the first part of the question may be regarded as decided: plants are able to take up and utilise the free nitrogen of the atmosphere.

But now comes the second problem; by what means is the nitrogen taken up and assimilated? It was proved by certain observers—Prof. Berthelot and HH. Hellriegel and Willfahrt—that the process depended on the activity of microbia. These minute beings were found on the surface of the soil, but more especially in nodules on the roots of leguminous plants, such as kidney-beans, peas, lupins, &c. It was found that those plants whose rootlets were most beset with these tubercles were least dependent upon nitrogenous manures, since by the mediation of the microbia they were able to draw their supply of nitrogen direct from the atmosphere. In some cases nitrates or ammoniacal compounds may interfere with the development and activity of the microbia, and thus hinder the growth of the crop. The lupins yield the best crop without the application of a nitrogenous manure, which if applied to them is wasted. Peas are less able to dispense with nitrogenous manures, as is also the case with clover.

But we can now take a third and final step. The action of the microbia to which we have referred is unquestionable, but it is not the only agency by which plants are able to appropriate atmospheric nitrogen. Franks has shown that plants other than leguminous are capable of effecting the fixation of nitrogen without the co-opera-

tion of microbia. He has cultivated oats, buckwheat, asparagus, colza, &c., in different soils, and finds that they can assimilate nitrogen without the aid of microbia, and of course without belonging to the leguminous class. They are able to produce organic nitrogen without impoverishing the soil, which, on the contrary, is rather enriched. Hence we see that Georges Ville's "sideration" is no subject for derision, but has its rational basis at once in practice and in Science.

ON THE MAGNETIC ELEMENTS FOUND IN ROCKS AND MINERALS.

By Dr. T. L. PHIPSON, F.C.S., &c.

IN addition to what has been stated on this subject by Prof. Liversidge in his interesting papers published recently in the *CHEMICAL NEWS*, perhaps I may be allowed to claim having first called attention to the presence of magnetite in the red hematite ore of Waldeck, Germany, as early as 1865. Since then I have many times found that the magnet extracts a notable amount of magnetic oxide from some English ironstones of a similar nature. But a more surprising result was obtained not very long ago whilst I was examining some Hungarian syenite rocks containing here and there specks of iron pyrites, and yielding to analysis a minute quantity of gold. From the pulverised rock the magnet extracted a dark coloured substance which dissolved in hydrochloric acid with evolution of hydrogen sulphide, and was proved to be magnetic pyrites.

I believe that a certain alloy of iron and platinum, said to exist in primitive rocks, can also be extracted in this manner. Rocks pulverised in iron mortars will almost always yield metallic iron particles in notable amount to the magnet, so that copper mortars must be used in such experiments.

Analytical Laboratory, Putney,
London, December 10, 1892.

NOTE ON MR. DOHERTY'S ANALYSIS OF THE BANANA.

By Dr. GEORGE LAWSON,
Professor of Chemistry, Dalhousie University, Halifax,
Nova Scotia.

MR. DOHERTY, of the Assay Department, New South Wales, has done good service in making and publishing, in the *CHEMICAL NEWS*, an analysis of the banana fruit. He shows that the peeled fruit of *Musa Cavendishii*, which contains 75.71 per cent of water, yields:—

Albumenoids	1.71 per cent.
Starch	5.90 ..
Sugar	3.00 ..
Carbonaceous matter ..	11.24 ..

An extension of Mr. Doherty's work into greater detail as regards the carbohydrates would be valuable.

From a chemico microscopical examination of the banana made many years ago (the notes of which have not been published), I ascertained that at the period of maturity of growth of the fruit (while still unripe) its constituent cells were densely filled with starch granules, which are elongated and of characteristic form. As the fruit ripened, the starch granules gradually disappeared, dissolving away into sugar, so that in the perfectly ripe fruit, or in the perfectly ripe pulpy portions of a fruit, there was little or no trace of visible starch. In other words, at the stage of simple maturity the carbohydrate cell-contents of the fruit consist entirely, or almost so, of

starch; while at perfect ripeness they are converted into sugar.

It would be interesting to have—(1) a careful determination of the actual amount of starch present in the mature fruit before commencement of the ripening process; and (2) a similar determination of the sugar at the period of perfect ripeness. The determinations should be made from fruits taken from the same bunch of the living plant. It does not grow here.

I presume Mr. Doherty's item—"carbonaceous matter (non-nitrogenous), 11.24"—represents principally cellulose, which seems large (in addition to woody-fibre, 1.74) for the peeled or pulpy part of such a succulent fruit, inasmuch as the starch and sugar together make scarcely 9 per cent. The proportion of sugar in the fruit at ripeness may be expected to be less relatively than the starch at the initial stage of ripening.

NEW METHOD OF PRODUCING GEMS ARTIFICIALLY.

By JAMES MORRIS, D.Sc.(Tüb.).

(Continued from p. 71).

In this article I shall deal further with the chief product of the process, namely, the crystals of alumina. In how far these crystals may be termed sapphires, or in how far only crystallised alumina, is not within the scope of the present paper.

It is known that the African diamonds differ in certain physical qualities from those of Brazil and India. When carbon crystals come to be produced artificially in numbers they will most probably differ physically from the products of all known mines. I presume that they would still be termed diamonds.

Towards aqueous solvents the crystals obtained by my process show great resistance, many of them having been heated in sulphuric acid for days. Towards fluxes they appear to be somewhat more easily attackable than would certain varieties of the natural stones, although the fact of their having been, in some cases, previously subjected to long heating in acid may have lowered their power of resistance.

On fusion with microcosmic salt they disappeared with very great difficulty. There was no appearance of silica. No great excess of salt was used. (The crystals had been previously tested both with hydrofluoric acid and with fluoride of ammonium). On fusion with borax they disappeared with rather more ease. The authorities vary in regard to the solubility of silica in borax. However, quite apart from the question of silica, the borax was used in many tests as being less liable to cause oxidation of the carbon in the crystals than microcosmic salt might have been.

This question of the carbon in the crystals,—carbon presumably in the diamond form,—is so remarkable that even on the evidence obtained I might hesitate to lay so much weight on it. I previously referred to the work of C. Greville Williams (*Proc. Roy. Soc.*, xxi., 1872-3, also in "Ures' Dictionary," and in *Encyc. Britt.*), and to the recent experiments of Luzi. The latter observer (*Ber. Deutsch. Chem. Gesell.*, 1891, p. 4093) heated mineral matter to fusion in contact with lamp-black, and he found on cooling that a portion of the carbon had assumed the form of graphite. He seemed to entertain the possibility of a real solution of the carbon in the mineral matter, with subsequent elimination in the graphitic form. It is at least possible that, under certain conditions of cooling, a portion of the carbon would have been retained in the mineral matter. In this communication Luzi brings the results of his experiments to bear on certain geological phenomena both general, specific, and local.

In a later paper (*Ber. Deutsch. Chem. Gesell.*, 1892, p.

2470), the same experimenter describes how he placed a diamond in a quantity of the "blue ground" (obtained from South Africa), and heated the latter to fusion. On subsequent examination he found that a large portion of the diamond had disappeared, and he did not seem to attribute such disappearance to any air which might have found its way to it, but to magmatic re-absorption. In this case, however, he entertains the possibility of the diamond carbon having been used to effect a reduction in the mineral matter.

Particles of graphite are found in gneiss, porphyrite, marble, and other rocks and rock masses. All this tends to show that the line of absolute insolubility is very difficult to determine.

I shall now proceed to one of the chief parts of the present communication, namely, the manner in which the crystals were obtained. The crystallising agent used was a very simple and natural one—to wit, carbonic acid gas, and at this point we go back to the first of all chemical-geological experiments.

About a hundred years ago Sir James Hall (*Trans. Roy. Soc., Edinburgh*, 1812, p. 71, 185), effected the transformation of limestone into marble, and the means which he used was the simple one of heating the substance in a closed vessel, and keeping the carbonic acid in. The object which he had primarily in view had nothing to do with mineral synthesis, so the considerations involved in this experiment need not be gone into at length here. He seemed, however, to regard the transformation as having been accompanied by actual fusion.

The experiment was repeated by Gustav Rose (*Mon. Ber. Berl. Akad.*, 1862, p. 669), by Becker (*Tschermak's Min. Mittheil.*, Heft i., 1885), and by Doelter (*N. J. F. Min.*, 1886, p. 133). The latter observer found that there was no real fusion, but a regeneration, and the last mentioned mineralogist got similar results by using not a closed vessel, but a tube open at one end and leading carbonic acid gas over the carbonate. Pressure is therefore not necessary. This last point is practically important. Similar experiments were successfully made with magnesite. The reason why carbonic acid gas effects the crystallisation of these carbonates, or of alumina, need not be considered at this stage.

In my experiments the gas was not made to act simply on the loose powder, but under the following conditions. Pure alumina was dissolved in pure hydrochloric acid, and a mixture of lamp-black and charcoal was added to the solution. The mass was evaporated, and the alumina was precipitated in the pores of the carbon. The mixture contained by weight rather more carbon than alumina. After further treatment to expel all the hydrochloric acid, the mixture was subjected to the action of carbonic acid gas at a red heat. The largest vessels used were the iron retorts which were formerly often employed in making oxygen gas from black oxide of manganese. They are about one foot high, and three or four inches wide. Very promising results were obtained in one inch iron tubes, heated in Fletcher tube furnaces. In this case the carbonic acid gas was heated alone before being passed over the mixture. The latter was, of course, also directly heated. In future working some equivalent disposition of the apparatus will be reverted to.

The mixture of alumina and carbon was at first rolled into balls, but as the retorts had to be opened at intervals for examination, the balls mostly broke down into fragments. This is a matter of mechanical arrangement. The lamp-black interlocked a large amount of the oxide, and the charcoal maintained the permeability to the gas. The gradual consumption of the carbon in the carbonic acid gas is, in an indirect way, equivalent to the removal of the solvent in cases of crystallisation from solution. By using a suitable mixture of lamp-black and charcoal, and by stopping the combustion at the proper point, the mass assumes a honeycombed structure which forms a matrix in which the alumina crystallises.

The best result was obtained on continuing the opera-

tion to what would be about the equivalent of one month's continuous heating. A very moderate red heat was employed. The factors of time and temperature are interchangeable within considerable limits, and in other cases crystals were obtained in very much less time. The experiments in the tubes proceeded rapidly. Many of the crystals obtained by the process were about 1 m.m. in diameter, some larger, and measurable crystals were found in thousands.

For an experimental process, often interrupted, and performed in extemporised apparatus, I think that the result may be pronounced distinctly favourable. Had experimental tube furnaces of proper size been obtainable I should not have used retorts.

Various precautions were taken in regard to the purity of the alumina, the acid, the carbon, and the carbonic acid gas. A very small amount of moisture in the gas seemed to be favourable. The carbon must be what could be termed "dry," that is, it must contain no tarry matter. There were in the product a few crystals which, from their shape, also from other considerations (reducing actions take place in the vessels), may possibly be a new oxide of aluminium. It is strange that no oxide corresponding to the magnetic oxide of iron has yet been found. Several observers have obtained indirect evidence of a lower oxide of aluminium having been formed, and its isolation is almost a certainty of the future.

There are many more interesting points connected with the chemical and physical, and more particularly crystallising, effects of carbonic acid gas, which I shall probably go into in a further communication.

In a paper of the present kind it is scarcely possible, and I certainly do not consider it desirable, to dissociate the chemical from the geological aspects of the question. One of the most important points of all is: in what degree, if at all, does the process described resemble the process of nature. In this connection we have the broad but still very relevant fact that carbonic acid is really found in many minerals, including quartz, topaz, and sapphire. I need hardly refer to all the literature, both special and allied, including the names of Brewster, Sorby, Simmler, Vogelsang, and many other and more recent observers. Certainly the fact cannot be overlooked that, in some of these crystals the carbonic acid is present in the liquid form.

In Quenstedt's "Mineralogie," article "Feldspath," he says (although it is not quite clear whether he speaks in his own name or quotes another author):—"Wasserporen mit beweglichen Bläschen in Feldspath des Basaltes von Lichtenberg in Franken (*Fahrh.*, 1867, p. 701), beweisen nur, dass auch im Feuer unter Druck Flüssigkeiten nicht fehlen." Professor Quenstedt was geologist, physicist, and mathematician. I do not know what attempts have been made to bring certain petrological phenomena into line with the known facts and accepted theories regarding temperatures, critical points, and pressures. As already stated in another sense, the factors of time and of temperature, also of pressure, seem to be largely interchangeable. Certainly Doelter's modification of Hall's original experiment shows that the importance of pressure may be overrated. It is quite possible that the rubies and sapphires of nature have been produced by more than one process.

Apart from the presence in various crystals of lacunæ, containing carbonic acid, the natural occurrence of the noble crystals of alumina is, in some cases, suggestive. According to Tennent, the matrix of the small rubies, mostly light coloured, found in Ceylon, is dolomite. Clear crystals, both blue and rose-coloured, are found in the saccharoidal dolomite at St. Gothard. Emery is found in granular limestones and dolomites in Naxos and other places.

The use of the carbon in my process may be less natural than the use of carbonic acid gas. Carbonaceous matter is not uncommon in rocks and minerals. It may also be that the carbon takes the place of one of the

undetermined physical factors which go to constitute the process of nature.

I venture to think that in the use of carbonic acid we have promise of a natural, simple, and effective instrument in unfolding certain problems in connection with the genesis and metamorphosis of many minerals. It also gives promise of the effectual synthesis of some of the noblest of them.

217, West George Street, Glasgow,
November, 1892.

THE ELECTROLYSIS OF METALLIC FORMATES.*

By HILL SLOANE WARWICK.

(Continued from p. 287).

Copper from Cadmium.

Copper taken.	Cadmium taken.	Metal deposited.	Free acid.	H ₂ O.	OH gas per min.	Time.	Diff. from theory.
Grm.	Grm.	Grm.	C.c.	C.c.	C.c.	Hrs.	Perct.
0.1074	0.0984	0.2061	10	100	0.8	17	—

This result was not unexpected, considering what we have already learned in regard to the behaviour of these metals. The deposit was very dark and spongy. Both metals were completely precipitated. Two subsequent experiments were equally unsatisfactory; in one the current was reduced to 0.3 c.c. OH gas per minute; in the other, 25 c.c. of formic acid was added. No separation was effected.

Copper from Iron.

Copper taken.	Iron taken.	Copper found.	Free acid.	H ₂ O.	OH gas per min.	Time.	Diff. from theory.
Grm.	Grm.	Grm.	C.c.	C.c.	C.c.	Hrs.	Perct.
1. 0.1057	0.1248	0.1035	25	125	0.8	20	—
2. 0.1057	0.1248	—	25	150	0.8	42	—
3. 0.1057	0.1248	0.1019	25	150	0.8	19	—
4. 0.1057	0.1248	0.0999	25	150	0.8	17	—
5. 0.1057	0.1248	0.1014	25	150	0.8	18	—

Although free acid was present in considerable quantity (25 c.c.), the formate of iron in the solution was decomposed with the formation of ferric hydrate, which separated as a light yellow froth on the surface of the solution. It also formed crusts at the edge of the copper deposit, which adhered to the dish with such tenacity that all attempts at removal by mechanical means were failures. Mere washing was without avail, and more energetic measures resulted in a loss of copper (1 and 4). Dilute hydrochloric acid was added to 2; but, while it dissolved traces of copper, it failed to remove the deposit of iron hydrate. Dilute sulphuric acid was also tried without success (3). In the final determination 20 c.c. of concentrated oxalic acid was added at the end of seventeen hours, and the current allowed to act one hour longer. The froth floating on the surface was dissolved, but the deposit on the copper was not appreciably affected. Except at the periphery the copper had a bright metallic lustre and was firm and adherent.

Cadmium from Iron.

Cadmium taken.	Iron taken.	Cadmium found.	Free acid.	H ₂ O.	OH gas per min.	Time.
Grm.	Grm.	Grms.	C.c.	C.c.	C.c.	Hrs.
1. 0.0984	0.1248	0.0996	25	150	0.8	23
2. 0.0984	0.1248	0.1021	25	150	0.8	45

The same trouble was experienced here. Similar attempts were made to remove the iron, but without

* Read before the American Philosophical Society, November 6, 1891. From the *Proceedings of the American Philosophical Society*, xxii, No. 136.

success. In the first of the above determinations 10 c.c. of oxalic acid solution was added before the conclusion of the experiment; in the latter, 20 c.c. of the same solution.

The hydrate of iron in the solution disappeared, but adherent crusts still remained on the surface of the cadmium.

Zinc from Iron.

Several tentative experiments were made, but as the iron showed the same tendency to separate on the sides of the dish, as in the preceding determinations, they were not continued.

Copper from Cobalt.

Copper taken.	Cobalt taken.	Copper found.	Free acid.	H ₂ O.	OH gas per min.	Time.	Diff. from theory.
Grm.	Grm.	Grm.	C.c.	C.c.	C.c.	Hrs.	Percent.
1. 0.1101	0.1080	0.1105	100	175	1	21	+0.36
2. 0.1101	0.1080	0.1095	100	175	1	17	-0.54
3. 0.1101	0.1080	0.1097	100	175	1	17	-0.36
4. 0.1101	0.1080	0.1107	100	175	1	18	+0.54
5. 0.1101	0.1080	0.1098	100	175	1.2	17	-0.27
6. 0.1101	0.1080	0.1097	100	175	1	16	-0.36

On attempting to prepare a solution of cobaltous formate for the above determinations, it was found that the salt made according to the method already described was not readily soluble in water. The solution was therefore prepared by double decomposition as follows:—500 c.c. of water containing 6.563 grms. of sodium formate was mixed with an equal amount of water in which 8.728 grains of cobalt chloride had been dissolved.

Of this solution 50 c.c. was taken, containing 0.1080 grms. of cobalt. The distance between the poles was 3.8 c.m., except 1 and 4, in which it was 2.8 c.m. Both of the latter were spongy; the others slightly so. As the conditions otherwise were similar, the difference in the character of the deposits was apparently due to the separation of the poles. Traces of cobalt were found in all the copper deposits. The copper was all out except in 3, 5, and 6, in which the solutions were coloured yellowish brown on the addition of hydrogen sulphide.

The copper deposit was dark in colour and adherent, although not very compact on the bottom of the dish.

Copper from Nickel.

Copper taken.	Nickel taken.	Copper found.	Free acid.	H ₂ O.	OH gas per min.	Time.	Diff. from theory.
Grm.	Grm.	Grm.	C.c.	C.c.	C.c.	Hrs.	Percent.
1. 0.1101	0.1028	0.1095	75	175	1	20	-0.54
2. 0.1101	0.1028	0.1097	100	175	1	17	-0.36
3. 0.1101	0.1028	0.1097	100	175	1	18	-0.36
4. 0.1101	0.1028	0.1098	100	175	1.2	17	-0.27
5. 0.1101	0.1028	0.1096	100	175	1	17	-0.46
6. 0.1101	0.1028	0.1098	100	175	1	17	-0.27

The same trouble was experienced in preparing a satisfactory solution of pure nickel formate as with cobalt, and it was found advisable to prepare the solution by double decomposition in the same way as the latter salt; 500 c.c. of this solution contained 8.3077 grms. of nickel chloride and 6.2469 grms. of sodium formate. In both cases a slight excess of sodium formate was used. The copper contained traces of nickel, and slightly coloured the solution when tested with hydrogen sulphide. The conditions were similar to those given under cobalt, and the results were quite as satisfactory. The copper was bright and compact.

(To be continued).

Determination of the Acidity of Milk.—H. C. Plaut (*Archiv. f. Hygiene*).—For determining the acidity of milk, the author prefers a modification of Soxhlet's original volumetric process. He titrates 50 c.c. of milk with $\frac{1}{2}$ normal solution of baryta, using phenolphthalein as indicator.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 1st, 1892.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

(Concluded from p. 300).

*75. "The Origin of Colour. VI. Azobenzene." By HENRY E. ARMSTRONG.

A compound represented by the formula $C_6H_5 \cdot N:N \cdot C_6H_5$ obviously does not come within my "colour rule," and should, in fact, be colourless; yet azobenzene is a brilliantly orange-red coloured substance; moreover, the formulæ usually attributed to the diazo-salts, e.g., diazobenzene chloride, $C_6H_5 \cdot N:N \cdot Cl$, represent these as comparable in constitution with azobenzene, yet they are colourless; hence I have long doubted the correctness of the formula attributed to azobenzene.

Werigo, in a paper, "Ueber die Additionsfähigkeit des Azobenzids" (*Annalen*, 1872, clxv., 189), has drawn attention to the readiness with which azobenzene forms addition compounds, and describes a hexabromide; he also states that it affords a colourless tetrabromo-substitution derivative. At my request, Mr. E. Mills has undertaken to revise Werigo's observations, and to study the bromo- and other derivatives of azobenzene in detail, as these promise to be of considerable interest.

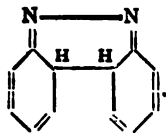
It appeared not improbable that Werigo's hexabromide belonged to the diazo-perbromide class, but this, it seems, is not the case; by treating it with ammonia, Mr. Mills has obtained only bromo-substitution derivatives of azobenzene—chiefly diparabromazobenzene—no azoimide being formed (*cf.* Meldola and Hawkins, *Proc. Chem. Soc.*, 1892, 133). He has confirmed Werigo's statement that when bromine acts on a hot alcoholic solution of azobenzene, a colourless tetrabromo-derivative is produced, which, on reduction, yields a tetrabromobenzidine apparently identical with that prepared from benzidine by Claus and Risler; and as he has not succeeded in obtaining the colourless tetrabromo-compound from diparabromazobenzene, there can be little doubt that none of the bromine atoms in the tetrabromo-derivative are in para-position to the nitrogen atoms.

Experiments made with the object of preparing alkyl derivatives of hydrazobenzene have hitherto been unsuccessful; when boiled with zinc chloride and alcohol it yields benzidine.

As the introduction of bromine into a coloured compound usually has the effect of heightening the colour, the conversion of azobenzene into a colourless bromo-derivative would seem to indicate that in some way the type changes; the tetra-derivative may well be a compound of the formula $C_6H_3Br_2 \cdot N \equiv N \cdot C_6H_3Br_2$.

The formula generally attributed to azobenzene may, therefore, be regarded as unsatisfactory not only because it is a coloured substance, but also because it combines with bromine, &c., with a readiness which is unusual in the case of mono-derivatives of benzene; because it yields a considerable proportion of a meta-monobromo-derivative, and of a higher bromo-derivative in which, apparently, none of the bromine atoms are in para-positions, an altogether unusual circumstance in the case of benzene mono-derivatives other than those containing acid radicles; and because it yields a colourless tetrabromo-derivative.

The following formula would "account" for all these peculiarities, and in a measure "explain" the formation of benzidine and diphenylene as well as the recent remarkable observations on the production of diphenylamine derivatives from azobenzenoid compounds on reduction; but it is eminently unconventional, and its adoption involves the recognition of a form of interaction not yet entertained by chemists:—

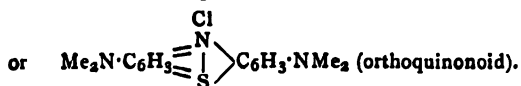


DISCUSSION.

Mr. GREEN considered that the relation of constitution to colour was a very important question both from a theoretical and practical point of view. The "quinonoid" hypothesis advocated by Dr. Armstrong appeared to him to be the only satisfactory attempt which had been hitherto made to formulate a complete theory of chromogenesis. Witt and others had given us chromophores, chromogens, and auxochromes, but these ideas were more names than theories, as no one had yet been able to predict what groups would be chromophores and what not. The "quinonoid" hypothesis, however, put us fairly on the road to predicting whether a compound of a certain constitution would be a dye-stuff or not, and might even eventually lead to the prediction of the shade and dyeing properties. He had given a good deal of attention to the subject recently, and although he had begun by regarding the "quinonoid" theory in a somewhat sceptical light, it had recommended itself to him more and more, as he found so many facts, hitherto inexplicable, which were explained perfectly simply by its means. He might instance the formation of rosaniline in the magenta-melt, which was readily explained by assuming the primary formation of an oxidation product of paratoluidine, viz., $\text{H}_2\text{C}:\text{C}_6\text{H}_4:\text{NH}$, which might then undergo alternate additions of aniline and reoxidations. He believed he had obtained this parent substance of the rosaniline series by oxidation of paratoluidine sulphate in acid solution, and it appeared to be identical with a substance described by Dr. Perkin as an isomer of parazotoluene. Again, the well-known tendency of quinones to form substituted amidoquinones with amines explains the ready formation of such complicated products as safranin, the indulines, aniline-black, &c.

He was inclined rather to attribute the cause of the colour in such "quinonoid" compounds to a strain set up within the benzene nucleus by two of the bonds ceasing to act centrally, than to the arrangement of these bonds outside the nucleus, i.e., as *intra-nuclear* rather than *inter-nuclear*.

On the "quinonoid" hypothesis, two groups of colours should be possible, viz., "ortho-colours" and "para-colours." The colours of the rosaniline series can only be formulated as para-colours, indigo only as an ortho-colour. On the other hand, many of the artificial colouring matters may be viewed either as para- or ortho-colours; thus methylene blue may be written:—



The speaker had recently examined a large number of colouring matters in regard to their behaviour towards reducing agents and the stability of their leuco-compounds, and had brought to light the remarkable fact that, whereas the leuco-compounds of the rosaniline, aurin, and phthalein colours were very stable, resisting air oxidation, the opposite was the case with the leuco-colours of the azine, oxazine, thiazine, acridine, safranin, and induline series, which all oxidise in the air to the corresponding colours with extreme rapidity. This was also the case with leucindigo and its sulphonic acid. The conclusion seemed to him to be irresistible, that the colours of the latter class were *ortho-colours*, whereas the eosines, aurines, rhodamines, &c., like the rosanilines, were *para-colours*.

Mr. FRISWELL agreed that confirmation of Dr. Armstrong's views was afforded by facts such as, for example, the colourlessness of triamidotriphenylcarbinol in comparison with the intense colour of its anhydro-base, which could be represented by a quinonoid formula. He, however, thought that the representation of colour as characteristic of a particular constitution was, for many reasons, to be deprecated, and that the remarkable effect of molecules external to the potential colour molecule in either developing or suppressing colour required attention. In the case of trihydroxytriphenylcarbinol, an apparently colourless substance, colour was developed by alkali, the salts being powerfully coloured; and in the case of the interesting dye "pure scarlet" discovered by E. C. Nicholson, which the speaker had himself studied, and which he thought was to be represented by the formula $\text{HO}:\text{C}(\text{C}_6\text{H}_4:\text{OH})_2(\text{C}_6\text{H}_3\text{MeNH}_2)$, both acid and alkali salts were coloured, although the substance itself was but feebly coloured.

The sulphonic acids of triphenylrosaniline were powerful colours, but their combinations with alkalies almost colourless; so that wool dyed with the sodium salt of Nicholson-blue was nearly white until dipped into acid. This phenomenon was even more marked in Meldola's alkali-green.

In illustration of the fact that substances exactly similar in constitution behaved in remarkably dissimilar ways, the following experiment was then made:—Two tubes were taken: one contained rosaniline base, benzoic acid, and aniline, the other triphenylrosaniline base, benzoic acid, and aniline—the latter being of an intense blue, the former a feeble red, colour. On heating to a similar temperature, the rosaniline base combined with the benzoic acid, and the well-known magenta colour was produced in the one tube; while in the other the triphenylrosaniline base split off from the benzoic acid, and only the dull brownish feeble colour of the base was noticeable. These facts showed:—(1) The importance of factors external to the potential colour molecule; (2) the variations of behaviour of substances containing similar potential colour molecules. Hence, he considered time not yet ripe for extensive generalisation as to the origin of colour in the benzene series.

[Mr. Friswell's argument is valid only if proof can be given that the coloured salts he refers to are *carbinotic*; there is no reason to suppose at present that the change which attends the formation of the rosaniline salts does not occur in all the cases he mentions in which coloured compounds result.—H. E. A.]

Mr. JACKSON enquired whether the vapour of quinone were coloured.

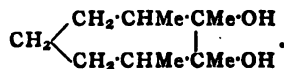
Mr. LING mentioned that diparaiodobenzene had but a pale yellow colour.

76. "The Reduction Products of Dimethyldiacetylpentane." By F. STANLEY KIPPING, Ph.D., D.Sc.

It is shown that dimethyldiacetylpentane,—



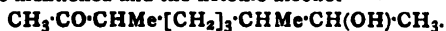
a diketone produced by the hydrolysis of ethylic dimethyldiacetylpinelate (Kipping and Mackenzie, C. S. Trans., 1891, 569), is readily converted by reduction into a mixture of approximately equal quantities of dimethyldihydroxynonane, and of a compound which, judging from the manner in which it is formed, may, it is thought, be regarded as tetramethyldihydroxyheptamethylene,—



When the crude products obtained by heating a moist ethereal solution of the ketone with sodium is submitted to steam distillation, a colourless oil, which has a peculiar and characteristic odour, slowly passes over, leaving as residue an almost odourless, practically non-volatile oil.

Excluding pinacones and other condensation products which might be formed, and which would be characterised

by a very high boiling point, only three compounds can be produced by the reduction of the diketone, namely, the above mentioned and the ketonic alcohol—



As the non volatile oil has the composition $\text{C}_{11}\text{H}_{24}\text{O}_2$, and yields a diacetyl derivative of the composition $\text{C}_{11}\text{H}_{22}\text{O}_2\text{Ac}_2$, it is to be regarded as dimethyldihydroxy-nonane.

The volatile oil is not reduced on treatment of its solution in moist ether with sodium, and is not acted on by phenylhydrazin or hydroxylamine; hence, it cannot be a ketonic alcohol of the constitution given above; it would appear probable, therefore, that it is a tetramethyldihydroxyheptamethylene. This conclusion is borne out by the great similarity in properties between the volatile oil and the dimethyldihydroxyheptamethylene previously described by Kipping and Perkin (*C. S. Trans.*, 1891, 214), a resemblance which cannot fail to be observed when working with the two compounds.

77. "The Products of the Interaction of Zinc Chloride or Sulphuric Acid and Camphor." (Third Notice). By HENRY E. ARMSTRONG and F. S. KIPPING.

In a previous notice (*Proc. C. S.*, 1892, 54), in which it was shown that the crude product obtained on heating camphor with either sulphuric acid or zinc chloride contains 1 : 2 : 4-acetylorthoxylene, reference was made to the presence of a constituent to which presumably the oil owes its strong, peppermint-like odour; all attempts to separate this constituent by fractional distillation were unsuccessful, nor could it be removed from the oil from which the acetorthoxylene-hydrazone had been separated by crystallisation. As it was observed that the crude oil readily decolourised an acid solution of permanganate, which has but little action on camphor and acetorthoxylene, a quantity of the oil from which these latter had, as far as possible, been separated was submitted to oxidation; ultimately an acid was obtained which has proved to be α -methylglutaric acid. As this acid is the characteristic oxidation product of the phorone obtained by distilling calcic camphorate, according to Königs and Eppen, which has a strong peppermint-like odour, it is very probable that a homologue of this phorone is present in the camphor product, which has a higher boiling point than camphorone.

79. "The Griess-Sandmeyer Interactions and Gattermann's Modification thereof." By HENRY E. ARMSTRONG and W. P. WYNNE.

Having frequently had occasion, during several years past, especially in the course of our studies of naphthalene derivatives, to avail ourselves of the marvellous improvements effected by Sandmeyer in the Griess methods of displacing the amido-group by halogens, &c., we have been led to carefully study the conditions requisite for success, and have long since come to the conclusion that, in very many cases, much better results may be obtained by operating at relatively low temperatures instead of at the boiling point as recommended in most cases by Sandmeyer. Experiments made at the request of one of the writers by Mr. Conroy with the object of comparing the yield in the case of the conversion of aniline into chloro- and cyano-benzene when operating:—

- 1, in accordance with Sandmeyer's original directions;
- 2, in accordance with Gattermann's directions, using finely-divided copper in place of cuprous salt;
- 3, in general accordance with Sandmeyer's directions, but at lower temperatures,

have led to the conclusion that, in the case of chlorobenzene, an infinitely better yield is obtained by mixing the cooled cuprous with the cooled diazo-solution, subsequently allowing the temperature to rise. It appears also that the Gattermann process affords a larger yield only in so far as it differs from the Sandmeyer process by being carried out at a lower temperature, and that it differs in no other essential particular from the Sandmeyer pro-

cess; there is, in fact, an entire absence of evidence that the copper acts as such, or except it has undergone conversion into cuprous salt. In the case of cyanobenzene, apparently the same advantage is not derived from carrying on the operation at a low temperature.

The "cold process" has been found to be of advantage in many other cases. Several years ago, the preparation of large quantities of orthochlorotoluene was carried out in the Central Institution Laboratory essentially in the manner described by Erdmann in his recent paper in *Liebig's Annalen*, and the yield was even better than that he obtained. Allusion is made to this in the paper by one of us on toluene derivatives (*cf. Proc. C. S.*, 1892, 139) which appears in the December number of the *Transactions*; several other instances of the application of the cold process are mentioned there.

We are entirely in accord with Erdmann as to the different and peculiar behaviour of the cuprous compounds of various diazo-derivatives; it is especially noteworthy in the case of naphthalene derivatives that the temperature at which nitrogen is evolved varies for each compound, and that there is a temperature optimum at which the conversion should be effected to obtain the maximum amount of pure product. There is no comparison, especially in the case of the naphthylaminesulphonic acids, between the two methods, colourless products being readily and almost immediately obtained by decomposing the diazo-cuprous compound at the favourable temperature, whereas on heating to the boiling point coloured products, which obstinately resist purification, are obtained. There can be little doubt that the formation of "azobenzenes," to which Erdmann directs attention, is, at least, very largely the cause of this colouration. The difficulty met with in converting betanaphthylamine into betachloronaphthalene, which Gattermann has specially noticed, is not got over by the cold process, a very large amount of a resinous condensation product being always formed; a method of obtaining a satisfactory yield of betachloronaphthalene directly from the amido-compound has yet to be discovered.

80. "Methods of Observing the Spectra of Easily Volatile Metals and their Salts, and of Separating their Spectra from those of the Alkaline Earths." By W. N. HARTLEY, F.R.S.

The difficulty in obtaining persistent flame spectra of lithium, potassium, rubidium, caesium, and thallium has to some extent been surmounted by the contrivances designed by Mitscherlich, Gouy, and others, but as solutions are necessary, these methods have not been found satisfactory by the author.

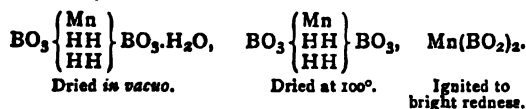
It is shown how flame colourations lasting for long periods may be obtained by converting the salts into fluosilicates, borates, or silicates. These compounds are less readily decomposed, and are more difficult to volatilise than the corresponding chlorides, sulphates, &c. Fused beads of the salts are held in the flame of a Bunsen burner on platinum wires, while measurements are made with the spectrometer.

When observing in the usual manner, the spectra of the alkalis are liable to be obscured by the presence of lines and bands due to the alkaline earths. By converting the material to be examined into a fluosilicate, borate, or silicate, the spectra of calcium, strontium, and barium are suppressed. If, however, the substance to be examined be converted into a borate, the alkali metals can first be observed, and subsequently by passing hydrogen chloride gas into the flame, the spectra of the alkaline earth metals become brilliantly visible. Although visible, the green bands due to boric oxide are feeble, and cause no confusion.

81. "Manganese Borate: its Constitution and Properties." By W. N. HARTLEY, F.R.S., and HUGH RAMAGE.

Particulars are given of the properties of manganese borate prepared in various ways from manganese sulphate and alkaline borates. Manganese borate dried *in vacuo*

over sulphuric acid is found to lose to the extent of 11.84 per cent of its weight water when heated at 100°; when heated from 100° to redness, it loses 19.65 per cent, which is water of constitution, the compound being a tetrahydric orthoborate, thus:—



By gradually heating the salt at fixed temperatures increasing to bright redness, and ascertaining the amount of water which it contained, a series of numbers was obtained from which a curve was drawn, the ordinate numbers being the percentages of water in the compound, and the abscissæ the corresponding temperatures. It was thus seen that there were five points above 100° at which dissociation was interrupted, and the compound in existence assumed a condition of stability. The following are the compounds of which the formation is inferred:—

Temp. of formation.	Formula of salt formed.	Water contained in compound.	
		Found.	Calculated.
22°	$\text{MnH}_4(\text{BO}_3)_2 \cdot \text{H}_2\text{O}$	26.86	27.69 per cent
100°	$\text{MnH}_4(\text{BO}_3)_2$	19.65	20.33 "
170°	$\text{MnH}_2\text{B}_2\text{O}_5$	11.45	11.32 "
195–220°	$\text{Mn}_{11}\text{H}_{20}\text{B}_{22}\text{O}_{54}$	10.43	10.40 "
255°	$\text{Mn}_6\text{H}_{10}\text{B}_{12}\text{O}_{29}$	9.71	9.61 "
295–305°	$\text{Mn}_3\text{H}_5\text{B}_6\text{O}_{14}$	7.20	7.84 "
Dull red heat	$\text{Mn}_2\text{H}_2\text{B}_4\text{O}_{17}$	2.87	3.09 "
Bright red	$\text{Mn}(\text{BO}_2)_2$	nil	
Partial fusion			

The solubility of manganese borate in various saline solutions was investigated; it was found to possess a maximum of solubility at or about 18°, and a minimum at 80°, so that when solutions are heated, they deposit the salt at this temperature.

It is believed that this is caused by the dehydration of the salt in solution, namely, $\text{MnH}_4(\text{BO}_3)_2 \cdot \text{H}_2\text{O}$, which becomes $\text{MnH}_4(\text{BO}_3)_2$, and this, being less soluble, is deposited: such a change being known to occur, and to be complete at 100° when the salt is heated in air.

AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Address by ALBERT B. PRESCOTT, Retiring President,
Delivered at the Rochester Meeting, 1892.

THE IMMEDIATE WORK IN CHEMICAL SCIENCE.

A DIVISION of science has a work of its own to do, a work that might well be done for its own sake, and still more must be done in payment of what is due to the other divisions. Each section of our Association has its just task, and fidelity to this is an obligation to all the sections. Those engaged in any labour of science owe a debt to the world at large, and can be called to give an account of what they are doing, and what they have to do, that the truth may be shown on all sides.

If it be in my power to make the annual address of this meeting of any service at all to you who hear it—in your loyalty to the Association—I would bring before you some account of the work that is wanted in the science of chemistry. Of what the chemists have done in the past the arts of industry speak more plainly than the words of any address. Of what chemists may do in the future it would be quite in vain that I should venture to predict. But of the nature of the work that is waiting in the chemical world at the present time I desire to say what I can, and I desire to speak in the interests of science in general. The interests of science, I am well

assured, cannot be held indifferent to the interests of the public at large.

It is not a small task to find out how the matter of the universe is made. The task is hard, not because of the great quantity in which matter exists, nor by reason of the multiplicity of the kinds and compounds of matter, but rather from the obscurity under which the actual composition of matter is hidden from man. The physicists reach a conclusion that matter is an array of molecules, little things, not so large as a millionth of a millimetre in size, and the formation of these they leave to the work of the chemists. The smallest objects dealt with in science, their most distinct activities, become known only by the widest exercise of inductive reason.

The realm of chemical action, the world within the molecules of matter, the abode of the chemical atoms, is indeed a new world and but little known. The speculative atoms of the ancients, mere mechanical divisions, prefiguring the molecules of modern science, yet gave no sign of the chemical atoms of this century, nor any account of what happens in a chemical change. A new field of knowledge was opened in 1774 by the discovery of oxygen, and entered upon in 1804 by the publications of Dalton, a region more remote and more difficult of access than was the unknown continent toward which Christopher Columbus set his sails three centuries earlier. The world within molecules has been open for only a hundred years. The Sixteenth Century was not long enough for an exploration of the continent of America, and the Nineteenth has not been long enough for the undertaking of the chemists. When four centuries of search shall have been made in the world of chemical formation, then science should be ready to meet a congress of nations, to rejoice with the chemist upon the issue of his task.

It is well known that chemical labour has not been barren of returns. The products of chemical action, numbering thousands of thousands, have been sifted, and measured, and weighed. If you ask what happens in a common chemical change, you can obtain direct answers. When coal burns in the air, how much oxygen is used up can be stated with a degree of exactness true to the first decimal of mass, perhaps to the second, yet questionable in the third. How much carbonic acid is made can be told in weight and in volume with approaching exactness. How much heat this chemical action is worth, how much light, how much electromotive force, what train-load of cars it can carry, how long it can make certain wheels go round,—for these questions chemists and physicists are ready. With how many metals carbonic acid will unite, how many ethers it can make into carbonates, into what classes of molecules a certain larger fragment of carbonic acid can be formed, the incomplete records of these things already run through a great many volumes. These carboxylic bodies are open to productive studies, stimulated by various sorts of inquiry and demands of life. Such have been the gatherings of research. They have been slowly drawn into order, more slowly interpreted to meaning. The advances have been constant, deliberate, sometimes in doubt, always persisting, and gradually gaining firmer ground. So chemistry has reached the *period of definition*. Its guiding theory has come to be realised.

"The atomic theory" has more and more plainly appeared to be the central and vital truth of chemical science. As a working hypothesis, it has directed abstruse research through difficult ways to open accomplishment in vivid reality. As a system of knowledge, it has more than kept pace with the rate of invention. As a philosophy, it is in touch with profound truth in physics, in the mineral kingdom, and in the functions of living bodies. As a language it has been a necessity of man in dealing with chemical events. Something might have been done, no doubt, without it, had it been possible to keep it out of the chemical mind. But with a knowledge of the primary elements of matter, as held at the beginning of

this century, some theory of chemical atoms was inevitable. And whatever theory might have been adapted, its use in investigation would have drawn it with a certainty into the essential features of the theory now established. It states the constitution of matter in terms that stand for things as they are made. The mathematician may choose the ratio of numerical notation, whether the ratio of ten or some other. But the chemist must find existing ratios of atomic and molecular mass, with such degree of exactness as he can attain. Chemical notation, the index of the atomic system, is imperfect, as science is incomplete. However defective, it is the resultant of a multitude of facts. The atomic theory has come to be more than facile language, more than lucid classification, more than working hypothesis; it is the definition of the known truth in the existence of matter.

The chemical atom is known, however, for what it does, rather than for what it is. It is known as a centre of action, a factor of influence, an agent of power. It is identified by its responses, and measured by its energies. Concealed as it is, each atom has given proof of its own part in the structure of a molecule. Proofs of position, not in space, but in action, as related to other atoms, have been obtained by a multitude of workers with the greatest advantage. The arrangement of the atoms in space, however, is another and later question, not involved in the general studies of structure. But even this question has arisen upon its own chemical evidences, for certain bodies, so that "the configuration" of the molecule has become an object of active research.

Known for what it does, the atom is not clearly known for what it is. Chemists, at any rate, are concerned mainly with what can be made out of atoms, not with what atoms can be made of. Whatever they are, and by whatever force or motion it is that they unite with each other, we define them by their effects. Through their effects they are classified in the rank and file of the periodic system. The physicists, however, do not stop short of the philosophical study of the atom itself. As a vibratory body its movements have been under mathematical calculations; as a vortex ring its pulsations have been assumed to agree with its combining power. As an operating magnet its interaction with other like magnets has been predicated as the method of valence. There are, as I am directly assured, physicists of penetration and prudence now looking with confidence to studies of the magnetic relations of atoms to each other.* Moreover, another company of workers, the chemists of geometric isomerism, assume a configuration of the atoms in accord with that of the molecule.

The stimulating truth of the atomic constitution of the molecule, a great truth in elastic touch with all science, excites numerous hypotheses, which, however profitable they may be, are to be stoutly held at a distance from the truth itself. Such are the hypotheses of molecular aggregation into crystals and other mineral forms. Such are the biological theories of molecules polymerising into cells, and of vitality as a chemical property of the molecule. Such are the questions of the nature of atoms, and the genesis of the elements as they are now known, questions on the border of meta-physics. Let all these be held distinct from the primary law of the atomic constitution of simple molecules in gaseous bodies, an essential principle in an exact science. The chemist should have the comfortable assurance, every day, as he plies his balance of precision, that the atom-made molecules are there, in their several ratios of quantity, however many unsettled questions may lie around about them. Knowledge of molecular structure makes chemistry a science, nourishing to the reason, giving dominion over matter, for beneficence to life.

Every chemical pursuit receives strength from every advance in the knowledge of the molecule. And to this

knowledge, none the less, every chemical pursuit contributes. The analysis of a mineral, whether done for economic ends or not, may furnish a distinct contribution toward atomic valence. The further examination of steel in the cables of a suspension-bridge is liable to lead to unexpected evidence upon polymeric unions. Rothamsted farm, where ten years is not a long time for the holding of an experiment, yields to us a classic history of the behaviour of nitrogen,—a history from which we correct our theories. The analysis of butter for its substitutes has done something to set us right upon the structure of the glycerides. Clinical inspection of the functions of the living body faintly finds a record of molecular transformations too difficult for the laboratory. The efforts of pharmaceutical manufacture stimulate new orders of chemical combination. The revision of the pharmacopoeia every ten years points out a humiliating number of scattered errors in the published constants on which science depends. The duty of the engineer, in his scrutiny of the quality of lubricating oils, brings a more critical inquiry into the laws of molecular movement. There is not time to mention the many professions and pursuits of men who contribute toward the principles of chemistry and hold a share therein. If it be the part of pure science to find the law of action in nature, it is the part of applied science both to contribute facts, and to put theory to the larger proof. In the words of one who has placed industry in the greatness of its debts to philosophic research, W. H. Perkin, "There is no chasm between pure and applied science, they do not even stand side by side, but are linked together." So in all branches of chemistry, whether it be termed applied or not, the best workers are the most strongly bound as one, in their dependence upon what is known of the structure of the molecule.

Studies of structure were never before so inviting. In this direction and in that especial opportunities appear. Moreover, the actual worker here and there breaks into unexpected paths of promise. Certainly the sugar group is presenting to the chemist an open way from simple alcohols on through to the cell substances of the vegetable world. And nothing anywhere could be more suggestive than the extremely simple unions of nitrogen lately discovered. They are likely to elucidate linkings of this element in great classes of carbon compounds, all significant in general chemistry. Then certain comparative studies have new attractions. As halogens have been upon trial side by side with each other, so, for instance, silicon must be put through its paces with carbon, and phosphorus with nitrogen. Presently, also, the limits of molecular mass, in polymers and in unions with water, are to be nearer approached from the chemical side, as well as from the side of physics, in that attractive but perplexing border ground between affinity and the states of aggregation.

Such is the extent and such the diversity of chemical labour at present that every man must put limits to the range of his study. The members of a society or section of chemistry, coming together to hear each other's researches, are better able, for the most part, to listen for instruction than for criticism. Still less prepared for hasty judgment are those who do not come together in societies at all. Even men of eminent learning must omit large parts of the subject, if it be permitted to speak of chemistry as a single subject. These considerations admonish us to be liberal. When metallurgical chemistry cultivates scepticism as to the work upon atomic closed chains, it is a culture not the most liberal. When a devotee of organic synthesis puts a low value upon analytic work, he takes a very narrow view of chemical studies. When the chemist who is in educational service disparages investigations done in industrial service, he exercises a pitiful brevity of wisdom.

The pride of pure science is justified in this, that its truth is for the nurture of man. And the ambition of industrial art is honoured in this, its skill gives strength to man. It is the obligation of science to bring the

* "The results of molecular physics point unmistakably to the atom as a magnet, in its chemical activities."—A. E. Dolbear, in a personal communication.

resources of the earth, its vegetation and its animal life, into the full service of man, making the knowledge of creation a rich portion of his inheritance, in mind and estate, in reason and in conduct, for life present and life to come. To know creation is to be taught of God.

I have spoken of the century of beginning chemical labour, and have referred to the divisions and specialities of chemical study. What can I say of the means of uniting the earlier and later years of the past, as well as the separated pursuits of the present, in one mobile working force? Societies of science are among these means, and it becomes us to magnify their office. For them, however, all that we can do is worth more than all we can say. And there are other means even more effective than associations. Most necessary of all the means of unification in science is the use of its literature.

It is by published communication that the worker is enabled to begin, not where the first investigation began, but where the last one left off. The enthusiast who lacks the patience to consult books, presuming to start anew all by himself in science, has need to get on faster than Antoine L. Lavoisier did when he began, an associate of the French Academy in 1768. He of immortal memory, after fifteen eventful years of momentous labour, reached only such a combustion of hydrogen as makes a very simple class experiment at present. But, however, early in chemical discovery, Lavoisier availed himself of contemporaries. They found oxygen, he learned oxidation. One great man was not enough in 1774, both to reveal this element and show what part it takes in the formation of matter. The honour of Lavoisier is by no means the less that he used the results of others; it might have been the more had he given their results a more explicit mention. Men of the largest original power make the most of the results of other men. Discoverers do not neglect previous achievement however it may appear in biography. The masters of science are under the limitations of their age. Had Joseph Priestley lived in the seventeenth century he had not discovered oxygen. Had August Kekulé worked in the period of Berzelius, some other man would have set forth the closed chain of carbon combination, and Kekulé, we may be sure, would have done something else to clarify chemistry. Such being the limitations of the masters, what contributions can be expected in this age from a worker who is without the literature of his subject?

In many a town some solitary thinker is toiling intensely over some self-imposed problem, devoting to it such sincerity and strength as should be of real service, while still he obtains no recognition. Working without books, unaware of memoirs on the theme he loves, he tries the task of many with the strength of one. Such as he sometimes send communications to this association. An earnest worker, his utter isolation is quite enough to convert him into a crank. To every solitary investigator I should desire to say, get to a library of your subject, learn how to use its literature, and possess yourself of what there is on the theme of your choice, or else determine to give it up altogether. You may get on very well without college laboratories, you can survive it if unable to reach the meetings of men of learning, you can do without the counsel of an authority, but you can hardly be a contributor in science except you gain the use of its literature.

First in importance to the investigator are the original memoirs of previous investigators. The chemical determinations of the century have been reported by their authors in the periodicals. The serials of the years, the continuous living repositories of all chemistry, at once the oldest and the latest of its publications, these must be accessible to the worker who would add to this science. A library for research is voluminous, and portions of it are said to be scarce, nevertheless it ought to be largely supplied. The laboratory itself is not more important than the library of science. In the public libraries of our cities, in all colleges now being established, the original

literature of science ought to be planted. It is a wholesome literature, at once a stimulant and a corrective of that impulse to discovery that is frequent among the people of this country. That a good deal of it is in foreign languages is hardly a disadvantage; there ought to be some exercise for the modern tongues that even the public high schools are teaching. That the sets of standard journals are getting out of print is a somewhat infirm objection. They have no right to be out of print in these days, when they give us twenty pages of blanket newspaper at breakfast, and offer us Scott's novels in full for less than the cost of a day's entertainment. As for the limited editions of the old sets, until reproduced by new types, they may be multiplied through photographic methods. When there is a due demand for the original literature of chemistry, a demand in accord with the prospective need for its use, the supply will come, let us believe, more nearly within the means of those who require it than it now does.

(To be continued).

NOTICES OF BOOKS.

Painters' Colours, Oils, and Varnishes. A Practical Manual. By GEORGE H. HURST, F.C.S., Member of the Society of Chemical Industry, &c. With numerous Illustrations. London: Charles Griffin and Co., Ltd., 1892. Small 8vo., pp. 461.

THE author of this work has most laudably and successfully sought to combine theory with practice. It is consequently neither a collection of recipes to be followed in blind confidence, and apt, under novel circumstances, to lead to disasters, nor yet a theoretical disquisition rich in proposals often inapplicable in practice. Mr. Hurst opens his work with an explanation of the different senses in which the term "colour" is often used. He compares the two theories of colours; the older, mainly developed by Brewster, accepting red, yellow, and blue as the three primary colours, and the new view of Young and Helmholtz which regards red, green, and violet as the primaries. Our author shows that the modern theory explains most accurately all the phenomena of colour as produced with the pure spectral rays, but that Brewster's theory is the more convenient if we come to work with pigments or dye-liquors never absolutely pure.

In the second chapter he proceeds to white pigments, beginning with white-lead, which, in spite of its objectionable properties, is still by far of all painters' colours the most largely used.

We do not find that the author fully defines the sense in which he uses the two terms "assay" and "analysis." We conclude that by the former he understands a search for impurities or adulterations, which may especially interfere with the use of the colour, and by the latter the full quantitative determination of all ingredients present.

In Chapter III. we are informed that Chinese vermilion is not made by the wet process commonly given, but by a dry method differing little from that employed in Europe. The superiority of the Chinese product is ascribed to the greater care taken by the Chinese in the manufacture. No decision is given as to the comparative beauty and permanence of vermillions made respectively by the wet and the dry processes.

Brilliant scarlet, otherwise known as "geranium red," is mercuric iodide. Though more beautiful than vermilion it is little used on account of its high price and its fugitive character. We have observed, however, that if obtained not by precipitation but by grinding the two ingredients together in the proper proportions, the pigment obtained is much more permanent. The act of combination is sometimes attended with a flash of light.

Hence caution might be requisite if this process came to be used on an industrial scale.

The directions for the manufacture and the use of the chrome yellows, oranges, and reds, are thoroughly practical. It is remarkable that the chrome yellows, known in the trade as "pure," contain lead sulphate produced by the presence of sodium sulphate or alum. The cheaper sorts contain china clay, baryta, or whiting.

A chrome colour which we do not find mentioned is stannic chromate, known as "pink colour." It has the colour of a light madder lake and is remarkably permanent. It seems to have been hitherto used exclusively in porcelain-painting. Much confusion has been produced by the multitudinous synonyms affixed to some of the chrome colours. Thus chrome-reds are known as Persian red, Derby red, American vermillion, Chinese red, Victoria red, &c. Some of these names are exceedingly objectionable.

A table here given as showing the composition of "pure" chrome colours is very interesting. A "pure primrose chrome" contains 36.5 per cent of lead sulphate and a "pure scarlet" 39.47 of white-lead. The ochres and siennas are very fully described. The ochre obtained from Shotover, in Oxfordshire, is the highest in quality. The order of the value of ochres, as judged by the prices which they command, is:—Oxford, 100; French, 33; Derbyshire and Welsh, 25; Irish and Devon, 20.

Field's "Mars pigments" are described as possessing no advantage over the natural ochres, &c., in brightness and permanence, whilst they have the disadvantage of being more expensive. Turner's yellow and Naples yellow are correctly described as nearly obsolete, whilst King's yellow is condemned as being strongly arsenical and therefore dangerous. We submit, indeed, that arsenical compounds should always be abandoned if any harmless product can be found to take their place. The origin of Indian yellow (purree) is correctly described. It is little used, as it is very fugitive.

Cadmium yellow receives the favourable opinion which it merits. The author states that he has not succeeded in obtaining the red modification of cadmium sulphide.

Among the Brunswick greens we must mention that most of the commercial samples are frauds, mere mixtures of chrome yellow and prussian blue, with barytes, gypsum, &c. The true Brunswick green, basic copper chloride, is now obsolete. Guignet's green is the best of the chrome greens, insoluble in acids and alkalies, and neither affecting other colours nor affected by them.

The arsenical greens are utterly to be condemned on account of their danger. Mention is here made as to the disputed character of emerald green, or Schweinfurth green, for which we may refer to the conflicting views of Dr. Jabez Hogg and of Prof. Galloway. It would seem that the effects of minute doses of arsenic, as in case of the air of rooms papered with arsenical hangings, depend to some extent on the idiosyncrasy of the inmates; but as we cannot foresee what may be the susceptibility of persons living or sleeping in such rooms, the only safety lies in the total renunciation of such pigments.

The lake colours are fully and satisfactorily described; both the old class, composed of a colouring-matter in combination with alumina, stannic oxide, &c., or the newer class, formed with the coal-tar colours. Many of the latter do not give good results as oil colours. With the exception, perhaps, of the alizarin compounds, the lakes of the coal-tar colours are not sufficiently permanent for the uses of the artist.

The chapter on the assay and analysis of pigments will prove most valuable, both to consumers and dealers, as will also the table showing the action of light on colours. The experiments, which were made by Captain Abney and Dr. W. J. Russell were extended over two years.

Space will not allow us to extend our survey of this useful book, but we feel bound to recommend it to all persons engaged in the arts concerned.

CORRESPONDENCE.

DISINFECTANTS—AN EXPLANATION.

To the Editor of the Chemical News.

SIR,—Dr. Klein's letter in the CHEMICAL NEWS, vol. lxxi., p. 304, necessitates a reply from me. It contains inaccuracies in its reference to "aminol" (with what it says of periodate crystals I am in no way concerned) which, if not promptly corrected, would do me injury.

1. The samples of "aminol" solution (strength 1 in 5000) to which Dr. Klein refers were sent to a number of medical men who had kindly consented to give it a trial in their practice. The reports so far received, which will be published in due course, record conspicuous successes, not only for this solution, but also of various dilutions thereof—even to 1 in 20,000.

2. Dr. Klein himself operated with a solution of the strength of 1 in 6000 in four out of the five series comprised in his experiments, and amongst the results obtained with it his report mentions the following:—

In Series IV.: "On *Staphylococcus aureus*, which may be taken as the most resistant microbe amongst those associated with surgical and other external disease processes, the 'aminol' solution (1 in 6000) did produce an effect, though a limited one, after two hours already, and after twenty-four hours' exposure destroyed the microbes."

In Series I.: "'Aminol' solution (1 in 6000) kills the *Bacillus Diptheriæ* in two hours. This was confirmed in Series III."

3. The "aminol" solution of the strength of 1 in 600, of which Dr. Klein's letter conveys the erroneous impression that it was the only one tested by him, was employed only in the fifth series. His statement of the disinfecting power of this strength is partly incorrect, partly misleading.

a. After twenty-four hours' exposure the growth of *Anthrax* spores was reduced from 100 to 6. That these remaining 6 would also have been eliminated after a little longer exposure (say another hour) will hardly be doubted, and that with a still more concentrated solution (say 1 in 400) complete disinfection would probably have been accomplished in a much shorter time than twenty-four hours (say eight to twelve hours) is certainly not an unreasonable assumption; nor should the possible enhanced effect of repeated applications be left out of sight in this connection. But after all, the question whether, and in what time, any strength of solution of "aminol" succeeds in destroying cultures of *Anthrax* spores is of no importance in medical practice. Dr. Klein himself, in the "Summary and Conclusions" of his report, points out "that the spores of *Bacillus Anthracis* may be left out of consideration, as they do not occur in the living body, and in infection with *Anthrax* generally the bacilli are always in the spore-free state, both in the blood and in the tissues."

b. Much more serious is the statement in Dr. Klein's letter, to the effect "that *Anthrax* bacilli, *Staphylococcus aureus*, and others were destroyed, but only after prolonged exposure." Now the facts, as recorded in Dr. Klein's report, are:—The four species of microbes operated upon besides *Anthrax* spores, and the results obtained, were the following:—

Sporeless <i>Bacillus Anthracis</i> , 1, 2, 8, 12, and 24 hours	No growth.
<i>Staphylococcus aureus</i> , 1 and 2 hrs.	Growth reduced one-half to one-third.
<i>Staphylococcus aureus</i> , 8, 12, and 24 hours	No growth.
<i>Bacillus Diptheriæ</i> , 1, 2, 8, 12, and 24 hours	No growth.
<i>Streptococcus Erysipelatis</i> , 1 and 2 hours	Growth reduced to one-half.
<i>Streptococcus Erysipelatis</i> , 8, 12, and 24 hours	No growth.

From the above it is evident that when Dr. Klein's letter was penned he had not at hand either his notes or a printed copy of his own report, which was published last year with his full approval,—I am, &c.,

HUGO WOLLHEIM.

101, Leadenhall Street, E.C.,
December 19, 1892.

THE POSITION OF CHEMISTS.

To the Editor of the Chemical News.

SIR,—I was much interested in Mr. Davis's letter which appeared in the *CHEMICAL NEWS* (vol. lxvi., p. 304). I know where a committee of a large corporation gas works in the Midlands offered £78 per annum for a competent chemist—which chemist was, moreover, to be under a manager who admitted that he was entirely ignorant of chemistry. The hours of the chemist were not short, from 9 a.m. till such time as his superior left him, often till 9 p.m.

Such a chemist must be a very meek individual, must show the best of results obtainable or unobtainable, for woe betide him should he bring the management of his superior (!) into question as the result of his work.

Now, in my humble opinion, night schools have done much to lower the standard of the salary of chemists. A case I know well, that of a young man following his trade of picture-frame making in the daytime, has elementary lessons in chemistry, and an hour's practical work for 20 or 30 evenings in the year, passes a not very formidable examination, and thus equipped, goes forth, not to benefit his picture-frame making, but to pose as an analytical chemist; and to obtain a footing, he will accept, nay, is proud of, a wage of £50 per annum. He is employed probably by a man who knows less chemistry than he himself does.

Failure to pass the examination as a pharmacist also adds to the number of analytical chemists of a low type. I know of instances where men have so failed and then fallen back on analytical work, and I do not think they are few and far between.

Another cause of the low salaries paid to chemists is brought about by chemical manufacturers constantly having fresh relays of youths in their laboratories, whom they paid nothing or at most only a nominal salary; and when a young man becomes fairly competent in the particular branch he is engaged in, he asks for his services to be rewarded, then he is told he is no longer wanted; as a rule, he cannot find employment in the same line, and having had no experience of any other, he is obliged to take a low salary like the picture-framer.

Now what must a person do who has had a college training for several years—perhaps taken an University Degree, obtained a thorough insight into the theory and practice of chemistry and its allied branches—unless he, too, accept £70 per annum? Otherwise he cannot, and I daresay does not, find employment.

I think that it would be well to commence with the oreigner when forming an Union, but I fear that little can be done, as the very men who are the cause of the complaint would join such a society as Mr. Davis indicates.—I am, &c.,

J. B. C.

December 19, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 23, December 5, 1892.

The Chemical Study of Opium-Smoking.—Henri Moissan.—The author sums up his results as follows.

There are two distinct cases; that where nothing is smoked but chandoo of very good quality, and where the smoke merely introduces into the lungs a very small quantity of morphia and of agreeable perfumes, and secondly that where the dregs or falsified opium are smoked which are decomposed not below 300°, with the formation of poisonous compounds such as pyrrol acetone and hydropyridic bases. We may compare this double action to the alcoholism produced in the one case by the repeated ingestion of a small quantity of alcohol of good quality, and in the other to the miserable state of the victims of absinthe. Arm. Gautier remarked that the most poisonous products of tobacco when smoked are hydropyridic bases.

Remarks on M. Barthe's recent Paper on the Volumetric Determination of the Alkaloids.—P. C. Plugge.—The author claims priority as against M. Barthe.

The Interchange of Carbonic Acid and Oxygen between Plants and the Atmosphere.—Th. Schloesing, jun.—The proportion of the volume of CO₂ which has disappeared to that of the oxygen which has appeared by the action of plants during the six or eight weeks of their growth, was found much below unity. In the third experiment the proportion did not appreciably vary in the course of vegetation. There enters into the composition of the organic matter of an entire plant a weight of hydrogen greater than that which would form water with the oxygen of this substance. The plant of the third experiment has derived oxygen to form its organic substance, not alone from the water and from the oxygen and the carbonic acid of the atmosphere, but also to a considerable extent from the oxygenous minerals of the salt. The green plant is a reduction apparatus.

Bulletin de la Société Chimique de Paris.
Vols. vii. and viii., No. 22.

This issue contains an account of the life and researches of Auguste Thomas Cahours, with a list of his published researches.

Congress on Chemical Nomenclature.—An account of the proceedings at the Geneva Conference, the particulars of which have been already published in the *CHEM. NEWS*.

Study of the Rate of Decomposition of the Diazo-Compounds.—J. Haussier and P. Th. Muller.—This memoir requires the accompanying diagram, figure, and tables.

MEETINGS FOR THE WEEK.

TUESDAY, 27th.—Royal Institution, 3. "Astronomy," by Sir Robert S. Ball, M.A., D.Sc., LL.D., F.R.S.
Photographic, 8.

WEDNESDAY, 28th.—British Astronomical Association, 3.

THURSDAY, 29th.—Royal Institution, 3. "Astronomy," by Sir Robert S. Ball, M.A., D.Sc., LL.D., F.R.S.

SATURDAY, 31st.—Royal Institution, 3. "Astronomy," by Sir Robert S. Ball, M.A., D.Sc., LL.D., F.R.S.

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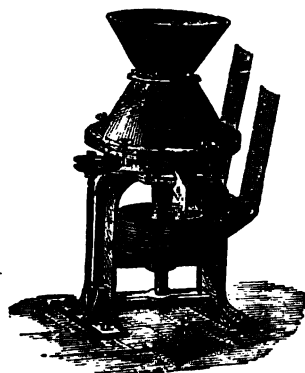
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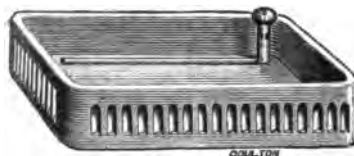
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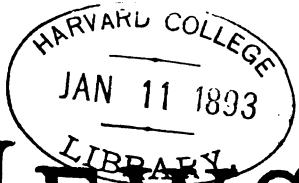
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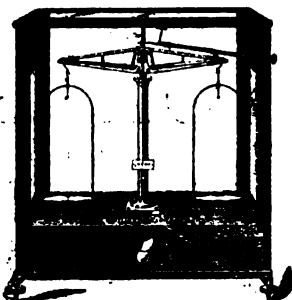
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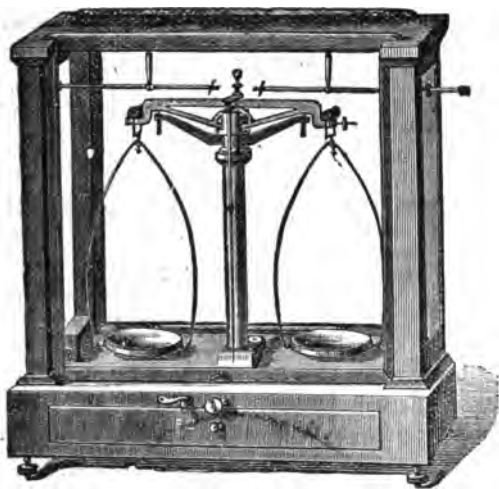


FIG. 3A.

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THE CHEMICAL NEWS.

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ON THE VELOCITY OF CROOKES'S CATHODE STREAM.*

By Lord. KELVIN, P.R.S.

In connection with his splendid discovery of the cathode stream (stream from the cathode in exhausted glass vessels subjected to electric force), Crookes found that when the whole of the stream, or a large part of the whole, is so directed as to fall on 2 or 3 sq. c.m. of the containing vessel, this part of the glass becomes rapidly heated up to many degrees, as much as 200° or 300° sometimes, above the temperature of the surroundings.

Let v be the velocity, in centimetres per second, of the cathode stream, and ρ the quantity of matter of all the molecules in 1 c.c. of it. Supposing that Crookes's experiments seem to prove to be not far from the truth, that their impact on the glass is like that of inelastic bodies, and that it spends all their translational energy in heating the glass. The energy thus spent, per square centimetre of surface struck, per second of time, is $\frac{1}{2}\rho v^2$; of which the equivalent in grm.-water-centigrade thermal units is approximately $\frac{1}{42,000,000}\rho v^2$. The initial rate at which this will warm the glass, in degrees centigrade per second, is—

$$\frac{\frac{1}{2}\rho v^2}{10^8 \times 42 \cdot 00} \dots \dots (1),$$

where σ denotes the specific heat of the glass, and a the thickness of it at the place where the stream strikes it.

The limiting temperature to which this will raise the glass is—

$$\frac{1}{E} \times \frac{\frac{1}{2}\rho v^2}{42,000,000} \dots \dots (2),$$

where E denotes the sum of the emissivities of the two surfaces of the glass in the actual circumstances.

It is probable that ρ differs considerably from the average density of the residual air in the enclosure. Let us take, however, for a conceivably possible example, $\rho = 10^{-8}$, which is what the mean density of the enclosed air would be if the vessel were exhausted to 8×10^{-6} of the ordinary atmospheric density.

To complete the example, take—

$$v = 100,000 \text{ c.m. per sec.}$$

(being about twice the average velocity of the molecules of ordinary air at ordinary temperature); and take—

$$\rho a = \frac{1}{2} \text{ c.m.,}$$

as it might be for an ordinary glass vacuum bulb; and take—

$$E = 20,000,$$

which may not be very far from the truth.

With these assumptions, we find, by (1) and (2) approximately, 1° per second for the initial rise, and 375° for the final temperature, which are not very unlike the results found in some of Crookes's experiments.

The pressure of the cathode stream of the velocity and density which we have assumed by way of example is ρv^2 , or 100 dynes per square centimetre, or about 100 m.grms. heaviness per square centimetre, which is ample for Crookes's wonderful mechanical results.

The very moderate velocity of 1 kilom. per second which we have assumed is much too small to show itself by the optical colour test. The fact that this test has been applied, and that no indication of velocity of the luminous molecules has been found, has, therefore, no validity as an objection against Crookes's doctrine of the cathode stream.

DESCRIPTION OF A NEW ELECTRIC FURNACE.

By HENRI MOISSAN.

THE discovery of the oxygen blast, by Henri Sainte-Claire Deville and Debray, rendered great services to chemistry. By means of this apparatus it has not only been easy to melt and refine platinum and to obtain new alloys, but also to extend and generalise a certain number of questions in mineral chemistry.

The temperature which may be reached with this apparatus fed with coal-gas and oxygen is about 2000°. We know that Deville and Debray found no substance except quicklime to resist this temperature.

Having had occasion in former researches to submit various substances to a temperature exceeding 2000°, I thought of utilising the heat yielded by the electric arc. After some trials I finally adopted the arrangement which I submit to the Academy, the only claim of which is its extreme simplicity.

This new furnace is formed of two bricks of quicklime, carefully cut and placed one above the other. The lower brick has a longitudinal groove which receives the two electrodes, and in the middle is a small cavity which serves as a crucible. This cavity may be more or less deep, and contains a layer, some centimetres in thickness, of the substance upon which the thermic energy of the arc is to act. Or we may also arrange a small crucible of charcoal containing the substance to be ignited. Or for the reduction of oxides and the subsequent fusion of the metals we use larger crucibles, and a cylindrical aperture made in the upper brick allows of throwing from time to time into the furnace small packets formed of a compressed mixture of oxide and of carbon. The furnace, therefore, receives merely a single arc, and the diameter of the carbons which serve as conductors will, of course, vary with the intensity of the current. After each experiment the ends of the carbons are entirely converted into graphite.

In our first researches we used a small Edison machine driven by a gas engine of four horse power. Most commonly the current traversing the furnace indicated 30 amperes and 55 volts. The temperature reached did not much exceed 2250°. In a second series of experiments we utilised the force produced by an eight horse-power gas-engine. The apparatus for measuring indicated 100 amperes and 45 volts. The temperature reached was about 2500°. Lastly, thanks to the kindness of M. Violle we were able to carry out our third series of experiments at the Conservatoire des Arts et Métiers. We had at our disposal a force of fifty horse-power, and the arc obtained under these conditions measured up to 450 amperes and 70 volts. The temperature was about 3000°. We are bound to address our thanks to M. Tresca, whose kind assistance proved very useful to us in this last series of experiments.

When employing high tension currents it is very useful to take certain precautions and to insulate the conductors with care. But even with currents of 30 amperes and 50 volts, such as those employed at the outset of these investigations, it is imperative not to expose the face to a prolonged action of the electric light, and always to protect the eyes with spectacles having very deep-coloured glasses. Electric sun-strokes were very frequent at the beginning of these researches; the irritation of the eyes produced by the arc may occasion very painful congestions.

The temperatures obtained in this series of experiments are only given approximately. But M. Violle, not content with furnishing the means to carry out this research, has kindly undertaken the special determination of those different temperatures by procedures which he will lay before the Academy at an early date.

When we became accustomed to the management of

* Read before the Royal Society, December 8, 1892.

this furnace we were able to produce a number of reactions which we will briefly summarise.

When the temperature is close upon 2500°, lime, strontia, and magnesia crystallise in a few minutes. If the temperature reaches 3000°, even the material of the furnace, quicklime, melts and flows like water. At the same temperature, carbon quickly reduces calcium oxide, and the metal is liberated in abundance. It readily combines with the carbons of the electrodes, forming a calcium carbide, liquid at a red heat, and easy to collect. Chromium sesquioxide and magnetic iron oxide melt rapidly at 2250°. Uranium sesquioxide if heated by itself is reduced to the state of black uranous oxide, forming long prisms. Uranium oxide, which cannot be reduced by charcoal at the highest temperatures of our furnaces, is quickly reduced at 3000°. In ten minutes it is easy to obtain an ingot of 120 grms. of uranium.

The oxides of nickel, cobalt, manganese, and chrome are reduced by charcoal at 2500° in a few moments. This is a fine experiment for a course of lectures, as it does not require more than from ten to fifteen minutes.

This method enables us easily to cause boron and silicon to react upon the metals and to obtain borides and silicides in very fine crystals. Lastly, it is easy under the above conditions to cause this elevated temperature to act upon a number of substances, simple and compound.

We are continuing this study, and shall soon communicate our further results to the Academy.—*Comptes Rendus*, cxv., p. 1031.

UNEXPECTED CHANGE IN THE CHARACTER OF A MINERAL WATER.

By W. P. MASON.

SOME years ago Prof. C. F. Chandler made an analysis of the water derived from the deep well situated at Round Lake, N.Y., a summer resort situated some fifteen miles south of Saratoga. At that time the well was 800 feet deep; the delivery, by pumping, good, and the quality of the water saline and very acceptable. It then analysed as follows, in grains per U.S. gallon:—

Sodium chloride	394.2943
Potassium chloride	9.4363
Sodium bromide	1.4716
Sodium iodide	1.3152
Sodium fluoride	trace
Lithium bicarbonate	2.7494
Sodium bicarbonate	48.9871
Magnesium bicarbonate	9.7846
Calcium bicarbonate	13.4457
Strontium bicarbonate	1.2038
Barium bicarbonate	0.5520
Iron bicarbonate	0.6344
Manganese bicarbonate	0.0768
Potassium sulphate	1.0275
Sodium phosphate	0.0228
Sodium borate	trace
Alumina	0.0346
Silica	1.2247
Organic matter	trace

486.2608

Some time since the owners, for reasons known to themselves, undertook to increase the output by sinking the well still deeper. Accordingly the boring was carried to a depth of 1400 feet, and a tube was inserted the entire length. The water obtained at this lower level was completely different from that previously furnished by the well, and at the same time quantities of gas, sufficient to light the premises, escaped from the tube. My analyses of both water and gas are appended:—

(Water results in grains per U.S. gallon).

Sodium sulphate	0.8584
Sodium chloride	15.7588
Sodium bicarbonate	86.0079
Sodium hyposulphite	0.0119
Sodium hydrosulphide	0.2345
Potassium sulphate	traces
Silica	0.3922
Oxide of iron and alumina	0.0619
Lithium bicarbonate	1.1313
Calcium carbonate	1.0966
Magnesium carbonate	0.9136

106.4671

The evolved gas consisted of—

	P.c. by volume.
Hydrogen sulphide	0.1
Oxygen	0.8
Carbon monoxide	0.3
Nitrogen	3.7
Methane	95.1

100.0

Rensselaer Polytechnic Institute,
Troy, N.Y.

STUDIES ON THE EARTHS OF THE CERIUM AND YTTRIUM GROUP.*

By A. BETTENDORFF.

(Concluded from p. 307).

THE double salt precipitated at the third treatment contained 1.240 grms. earth, having the equivalent $RO=119.83$, which in the state of nitrate showed the absorption lines of samarium very faintly. The gadolinia which remained in solution on the treatments I., II., and III., in the state of nitrate as a syrupy solution of the depth of 0.1 metre, gave only slight indications of samarium; there was not a trace present of other absorption lines. The close agreement of the equivalent of the three fractions, as well as the approximately accordant solubility of the gadolinium-potassium sulphate in a saturated solution of potassium sulphate, allow us to infer the unity and the purity of the three fractions. This assumption is confirmed by the circumstance that a portion of the earth weighing 1.57 grms. obtained from a mixture of the three fractions by partially precipitating the nitrate with dilute ammonia, gave the equivalent $RO=120.19$. As the mean value obtained for gadolinia we should have the equivalent $RO=120.18$, $R_2O_3=360.54$, whence the resulting atomic weight of gadolinium is $R=104.22$, III. $R=156.33$. Gadolinia, if strongly ignited, is nearly white powder with a slight yellowish cast. It is easily dissolved by acids, and yields perfectly colourless salts. If slightly heated in a current of hydrogen it becomes perfectly white without any change of weight. If very intensely ignited in the same current it seems to undergo a partial reduction, as it takes a very tender, grey cast, with a slight loss of weight of 0.11 per cent. This grey cast disappears again on heating in a current of air. 1.1874 grms. gadolinia, after intense ignition in a porcelain tube filled with hydrogen, weighed only 1.1860 grms.

After heating in a current of air the original weight was again obtained. If the grey earth is treated with very dilute hydrochloric acid, avoiding any rise of temperature, there is left a small residue of a dark colour. The earth which has passed into solution, if separated by oxalic acid and ignited, on renewed treatment with hydrogen becomes again a light grey. By frequent repetition we may obtain a rather larger quantity of this grey

* From *Liebig's Annalen*.

substance. On ignition in air it yields gadolinia of the same colour and the same equivalent as the material originally used for the experiment. 0.6281 grm. oxide yielded 1.0454 sulphate, $RO = 120.20$.

Gadolinia, if heated in air to bright redness, exhibits in a vacuum intense fiery red cathodic luminescence. Its spectrum consists of an orange-red line, very bright and sharp, the middle of which falls at the wave-length $\mu\mu$ 6094. It is well suited for the recognition of gadolinia. There are also indications of bands which, however, on account of their extremely feeble illumination, admit only of approximate measurements. I give them in the following conspectus:—

$\lambda = \mu\mu$ 6282.	Middle of an extremely faint band.
" " 6094.	Middle of an intensely bright, narrow, orange-red band.
" " 5925.	Indication of a narrow band.
" " 5860.	" " "
" " 5800.	" " "
" " 5745.	Beginning of an extremely faint band, which gradually vanishes.
" " 5502.	Indication of a narrow band.
" " 5420.	" " "
" " 5320.	" " "

From here onwards the spectrum becomes continuous, decreasing in intensity, and vanishes at $\lambda = \mu\mu$ 4810.

The luminescence band, $\lambda = \mu\mu$ 6094, has been previously observed by W. Crookes in a mixture of yttria and samaria. He characterised it then as an anomalous line, and believed it must be attributed to samaria. Subsequent experiments showed him that samaria prepared from gadolinite did not show this band, and that it appears only in those earths of samarskite which immediately follow samaria on a systematic decomposition by fractionated precipitation with ammonia. W. Crookes now ascribed this band to a new element in samarskite. Previously he had described a luminescence spectrum of the then unknown earth Y_e (gadolinia), and given a drawing of it, in which, along with other sharper and brighter bands, the line 6094 was laid down. He regards the bands $\lambda = \mu\mu$ 5410 and 5450 as characteristic of gadolinia.

On the spark spectrum of gadolinium chloride we have only a communication by Lecoq de Boisbaudran. He describes it as composed of a great number of faint bands with separate bright lines, and gives precise measurements of their wave-lengths. I have never been able to obtain this spark spectrum, although I, finding myself thus disagreeing with so prominent and experienced a spectroscopist, spared neither time nor trouble. My gadolinia, $RO = 120.18$, as a chlorine compound gives neither lines nor bands, whether in concentrated or dilute aqueous solutions, at the most different spark-lengths of a very powerful spark-inductor. At a distance of about 3 m.m. of carbons saturated with the concentrated chlorides there sometimes appear in the green part of the spectrum indications of single lines, but careful measurements proved that they were due to traces of samaria, which I had not been able to eliminate from my preparation of gadolinite earths.

THE ANALYSIS OF FERROCHROME, FERRO-ALUMINIUM, FERROTUNGSTEN, FERROSILICON, AND FERROTITANIUM.*

By A. ZIEGLER.

(Concluded from p. 296).

THE opening up of ferroaluminium and the determination of the accompanying elements is effected essentially in the same manner as that described for ferrochrome. The quantity of the sifted material used is from $\frac{1}{2}$ to 1 grm.

* From the *Zeit. Anal. Chemie*.

Ferroaluminium, in consequence of its larger proportion of iron, requires rather more prolonged fusion than ferrochrome. It is advantageous to apply heat whilst dissolving the melt in water. Of course, with ferroaluminium no carbonic acid is introduced after the melt is dissolved, and the solution is not evaporated to dryness lest the sodium aluminate formed should be decomposed. On the contrary, it is well to add a little alkaline hydroxide whilst dissolving. On dissolving the residue of the melt in hydrochloric acid after extraction in water, any portions which have not been opened up require particular attention. The first separation of the aluminium from the bulk of the alkalis in the filtrate of the solution of the melt can also be very well effected without the introduction of carbonic acid by an accurate neutralisation with hydrochloric acid and the application of heat.

Ziegler recommends likewise the following method for the analysis of ferroaluminium. He dissolves $\frac{1}{2}$ grm. of the substance in powder or borings in the quantity of hydrochloric acid (1 : 3) required for solution in a platinum capsule (1), evaporates to dryness, melts with an excess of sodium carbonate or potash-soda, and proceeds with the aqueous solution of the melt for the determination of the aluminium after the separation of the silica substantially as described for the determination of chrome. But we may also, as it is preferable, introduce the desiccated hydrochloric solution into the silver crucible by means of a moistened filter, free from ash, and effect here the separation completely by fusion with six parts sodium hydroxide and three parts soda-salt-petre.

In other respects we proceed as directed for the analysis of ferrochrome.

If iron is still present in the precipitate of alumina, which may be perceived by its yellowish colour, after ignition it may be dissolved by fusion with bisulphate free from iron; the iron after reduction may be titrated with zinc, free from iron, and deducted as ferric oxide. Aluminium may also be freed from any trace of iron by repeated fusion with soda. Ferrotungsten may be likewise opened up by fusion with caustic alkali and an alkaline nitrate in a silver crucible, and in the further analysis all the points laid down under ferrochrome must be observed.

The proposed flux is also suitable for opening up ferro-silicon. But ferrosilicon may be quite as well decomposed by fusion with sodium bisulphate in a platinum crucible. The silica remaining after treatment with water is filtered off, and after weighing volatilised with hydrofluoric and sulphuric acids. This latter method, according to Ziegler, can be considered unobjectionable only if it is established that during this process no trace of silicon is lost as silicon hydride.

Ferrotitanium cannot be sufficiently decomposed with the flux above mentioned. The following method yields results which are technically satisfactory. One-half grm. of the alloy, pulverised and sifted, are opened up with sodium bisulphate exactly in the same manner as directed for ferrochrome, but the melt is dissolved in cold water. The residue, if no undecomposed substance is present (in which case the fusion must be repeated) must be evaporated off with hydrofluoric and sulphuric acids, whereby the silica is determined. Any essential residue is once more opened up with sodium bisulphate and added to the main solution. This is now diluted to about 1 litre, neutralised with ammonia, and mixed with an aqueous solution of sulphurous acid. It is then slowly heated to ebullition and boiled (covered), replacing the evaporated water if needed for one and a half to two hours.

If we operate in this manner almost all the iron remains in solution as a ferrous salt at the first precipitation. The precipitate is filtered, if necessary, through a double filter, and washed with acetic acid at about 4 per cent. The filtrate must be absolutely clear. It is then nearly neutralised with ammonia, mixed with aqueous sulphurous acid, and boiled for an hour as a check on complete precipitation.

The first precipitate of hydrated metatitanic acid (still

containing iron), is evaporated to dryness, opened up with bisulphate, and treated in the same manner as the solution from the first opening up. If the operation is properly conducted the second precipitation gives a pure white precipitate of titanic acid containing mere traces of iron. If iron is present in a larger quantity, the opening up and precipitation are repeated. The precipitate thus obtained after incineration, treatment with ammonium carbonate, and sufficient ignition is pale, greyish brown titanic acid, which, on ignition, appears deep lemon-yellow, almost orange.

In the determination of titanic acid the author calls attention to the following points. If the liquid passes the filter in a turbid state, the addition of ammonium chloride is beneficial; or the precipitate may be mixed up with the paper of a filter containing a known proportion of ash. Hydrated titanic acid retains sulphuric acid obstinately, whence the incinerated precipitate must be cautiously heated with ammonium carbonate.

Half a grm. ferrotitanium is decomposed in about two hours on gentle heating with aqueous hydrofluoric acid. Melting soda-salt-petre does not take up any titanium from ferrotitanium. This alloy is imperfectly decomposed by hydrochloric, nitric acid, and *aqua regia*.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING NOVEMBER 30TH, 1892.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, December 7th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 181 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from November 1st to November 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

As pointed out by anticipation in our report for September, the lowness of the average proportion of organic matter present in the Metropolitan water supply for many months past could not, with the abundant fall of the leaf, and greater or less stagnation of fluvial vegetation attendant on the coming of winter, be expected to be much longer maintained. It was indeed well maintained during the month of October, but in the case of the supplies furnished by each of the seven Companies during the past month of November, there was a noticeable increase in the proportion of organic matter present in the water, as indicated alike by the estimations of organic carbon, of oxygen required for oxidation, and of degree of colour tint.

In the case of the Thames-derived water, for example, the mean amount of organic carbon in the supply for the month was found to be 0.204 part, and the maximum amount in any single sample examined 0.285 part in

100,000 parts of the water, as against a mean of 0.117 part, and a maximum of 0.155 part per 100,000 parts of water in the previous six months' supply, the mean increase, though relatively large, amounting indeed to an absolute addition of only 0.087 part of organic carbon in 100,000 parts of the water, corresponding as nearly as may be to an addition of about one-sixth of a grain of organic matter per gallon.

The vegetable origin, moreover, of this small additional amount of organic matter is inferable from the fact that, while the mean ratio of carbon to nitrogen in the minute proportion of organic matter present in the supply during the previous six months was as 100 : 27.1, the mean ratio in the larger proportion present in the November supply was as 100 : 19.8; or, inferentially, the ratio of carbon to nitrogen in the excess of organic matter present in the November supply was as 100 : 9.4 only.

Of the 182 samples of water examined by us during the past month, the entire number were found to be well-filtered, clear, and bright. The flooded state of the rivers at the beginning of the month, consequent on the heavy rainfall during the last days of October, was altogether without noticeable effect on the character of the water supply. Throughout November there was no heavy rainfall, and the total fall was slightly below the average.

We are, Sir,

Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.

OBSERVATIONS ON FERRO-TUNGSTEN.*

By WM. H. WAHL.

In the course of an investigation carried on during the past two years by the writer, in conjunction with Dr. William H. Greene, with the object in view of producing pure ferro-alloys, we made a number of experiments with ferro-tungsten.

These tungsten alloys exhibited similar physical properties, possessing considerable hardness and toughness, an extremely fine crystalline texture, with a fracture resembling that of tool-steel, and a specific gravity ranging between 9.3 and 10.14.

Some of the fractures, however, exhibited the fact that the alloy was not entirely homogeneous, disclosing under the glass and in places to the eye the presence of what are apparently smooth cleavages of imperfect crystals scattered through the finely-crystalline matrix of the alloy. The specimen shown you will illustrate my statement.

A sample of the alloy of 10.14 specific gravity was analysed at my suggestion by Mr. J. F. de Benneville in the laboratory of Dr. Genth. The result of the analysis exhibited a very high percentage of tungsten in the sample, and its behaviour towards liquid and fused solvents proved the interesting fact that a large proportion of the tungsten was present in the uncombined condition, as metallic tungsten, crystallised in the matrix of the alloy. The facts upon which Mr. de Benneville has founded this observation will appear in the following extract from a letter describing briefly the method pursued in his analytical work:—

"Aqua regia attacked it, although not energetically, and by decanting and adding fresh portions of acid from time to time a residue was obtained which resisted further action by acids, or by fusion with Na_2CO_3 and KNO_3 . It was a heavy, black, pulverulent substance, and in its negative action towards solvents answered to tungsten, which I took it to be. It gave 22.54 per cent of the original material. A second portion of the material

* Read at the Meeting of the Chemical Section of the Franklin Institute, November 15, 1892.

(powdered in a steel mortar) was fused with a mixture of Na_2CO_3 and KNO_3 , lixiviated, and the residue weighed. This was fused again and the residue weighed, the second weighing being practically the same, and yielding 22.80 per cent of the original material. Using strong HCl (1.20 sp. gr.) in successive portions, decanting, igniting the residue, and treating again with acid, gave me 21.74 per cent."

The foregoing extract appears fully to justify the conclusion that the undissolved residue represents the metallic tungsten present in the alloy in the uncombined state.

The composition of the metal analysed by Mr. de Benneville is as follows:—

	Per cent.
C	0.85
P	0.041
Si	0.14
Mn	trace
Fe	42.28
W (metal)	22.54
W (alloy)	34.35

100.201

A study of these figures reveals another interesting fact to which I desire to call your attention.

Taking the figures of the iron and combined tungsten (42.28 : 34.35) and calculating the percentage of tungsten which this ratio represents, we obtain 44.82 per cent tungsten. A calculation shows also that the figures representing the compound Fe_3W are almost identical with the ratio above named, to wit:—

Fe_3W found. Per cent.		Fe_3W by theory. Per cent.		Difference.
Fe	W	Fe	W	
55.18	44.82	54.91	45.09	—0.27
100.00		100.00		

The conclusion would seem to be justified by the facts above noted, that the saturation point of iron for tungsten is represented by the ratio exhibited in the compound Fe_3W , and that any excess of tungsten, above this ratio, present in a tungsten iron will remain uncombined.

I wish to express this statement as *probably* the correct interpretation of the facts, for it is hazardous to make a generalisation of this kind on the results of a single analysis.

It may be interesting to note in conclusion that Howe, in his "Metallurgy of Steel," refers to several cases of ferro-tungsten indicating the composition Fe_3W , and that the works on metallurgy as a rule accept without question the dictum that iron and tungsten will unite in all proportions. In the light of the facts given in this paper, this last statement requires qualification.

THE ELECTROLYSIS OF METALLIC FORMATES.*

By HILL SLOANE WARWICK.

(Concluded from p. 311).

Cadmium from Cobalt.

Cadmium taken.	Cobalt taken.	Cadmium found.	Free acid.	H_2O .	OH gas per min.	Time.	Diff. from theory.
Grm.	Grm.	Grm.	C.c.	C.c.	C.c.	Hrs.	Perct.
1. 0.0984	0.1080	—	25	100	0.5	22	—
2. 0.0984	0.1080	—	25	150	0.8	45	—
3. 0.0984	0.1080	—	50	150	1.5	18	—

It was naturally expected that cadmium would be completely precipitated from cobalt and nickel by employing a weak current, but from an examination of the above results it will be seen that a separation was not accomplished.

Even with a current of 1.5 c.c. OH gas per minute, the cadmium failed to deposit completely and was contaminated with cobalt (3). It was very spongy, and the solution still contained cadmium at the expiration of twenty-two hours. The current was then increased and allowed to act for forty-five hours (2). Cadmium was found in the solution, cobalt in the deposit. The distance between the electrodes was 2.8 c.m.

Cadmium from Nickel.

Cadmium taken.	Nickel taken.	Cadmium found.	Free acid.	H_2O .	OH gas per min.	Time.	Diff. from theory.
Grm.	Grm.	Grm.	C.c.	C.c.	C.c.	Hrs.	Perct.
1. 0.0984	0.1028	0.0758	35	150	0.5	19	—
2. 0.0984	0.1028	0.1045	35	150	1.5	21	—
3. 0.0984	0.1028	0.1348	50	125	1.5	17	—

The results were quite as unsatisfactory as with cobalt. Cadmium was found in all three solutions, and more or less nickel was found in the deposits. In 3 the nickel came out as a grey deposit on the cadmium. The deposit was firm and adherent, although dark in colour. The distance between the electrodes was 2.5 c.m., except 3, in which the pole separation was 2.8 c.m.

Zinc from Cobalt.

Zinc present.	Cobalt present.	Zinc found.	Free acid.	H_2O .	OH gas per min.	Time.	Diff. from theory.
Grm.	Grm.	Grm.	C.c.	C.c.	C.c.	Hrs.	Perct.
1. 0.1006	0.1080	—	50	175	3	17	—
2. 0.1006	0.1080	—	100	175	5	18	—

Zinc from Nickel.

Zinc present.	Nickel present.	Zinc found.	Free acid.	H_2O .	OH gas per min.	Time.	Diff. from theory.
Grm.	Grm.	Grm.	C.c.	C.c.	C.c.	Hrs.	Perct.
3. 0.1006	0.1028	—	50	175	2.7	18	—
4. 0.1006	0.1028	—	100	175	5	18	—

2 and 4 were performed under similar conditions. The distance between the poles was 2.2 c.m. The current was generated by a battery of Bunsen cells. Even with a current of 5 c.c. gas per minute zinc was found in the solution in traces, while considerable quantities of cobalt and nickel separated as a coating upon the cadmium. 1 and 3 were also failures. A separation was not obtained even approximately.

Summary.

As a result of the foregoing experiments, it was found that the amount of copper, cadmium, or zinc deposited in a given time was proportional to the strength of the solution, and that the presence of free acid in moderate quantity did not materially affect the result.

Increasing the distance between the poles resulted in diminishing the amount of metal deposited, but the rate of decrease diminished as the distance between the electrodes increased.

Elevation of temperature caused an increase in the amount of metal deposited, the rate of increase being greatest at 80° in neutral and acid copper solutions, and at 60° in cadmium solutions containing free acid. On the other hand, the amount of zinc deposited in solutions to which free acid had been added diminished as the temperature rose, nothing being deposited at 80°.

Attempts to secure compact and adherent deposits of cadmium and zinc in neutral solutions were failures.

In acid solution copper and cadmium separated completely and satisfactorily. The zinc deposits were spongy, but the precipitation was complete.

* Read before the American Philosophical Society, November 6, 1891. From the *Proceedings of the American Philosophical Society*, xxi., No. 136.

Lead was mainly deposited on the negative pole, both in neutral and acid solutions. Manganese was precipitated on both poles, but the amount of peroxide separating on the cathode was reduced to mere traces by the presence of free acid.

The following separations were satisfactorily accomplished:—Copper from zinc, cobalt, and nickel, and cadmium from zinc and manganese.

Attempts to deposit copper in the presence of iron and cadmium, and zinc in the presence of iron, cobalt, and nickel, were successful. Nor was it possible in the presence of the last three metals named to estimate cadmium.

In conclusion I wish to express my obligations to Prof. Edgar F. Smith, at whose suggestion the work was undertaken. To his supervision and advice is largely due whatever value may attach to these results.

A RAPID METHOD FOR PHOSPHORUS DETERMINATION IN IRON, STEEL, AND ORES.*

By JAMES O. HANDY,
Chemist of the Pittsburgh Testing Laboratory.

No method of determining phosphorus will find favour among chemists unless it possesses advantages over existing methods. While retaining the accuracy of the best methods now known, it must be simpler, more rapidly executed, or less expensive. My belief that the process which I have worked out is a step in this direction is my reason for now describing it.

I owe to Mr. C. E. Manby's paper, in the *Y. A. and A. C.* for February, 1892, the suggestion of essential points in my process. The method which he gives is too long, and would not compete with the Emmerton-Drown-Jones method (*A. I. M. E.*, February, 1890), which can be executed, with proper appliances, in thirty minutes, or less. Mr. E. F. Wood's latest method, a gravimetric one, is said to yield results in twenty minutes. I do not know how uniformly reliable these results are. I believe that they are always checked by a longer method.

I have proved by a great many experiments that several of the steps of Mr. Manby's process can either be safely dropped or simply modified, and a rapid and satisfactory process produced.

My method consists of the following points:—

(a). Separation of the phosphorus as pure phospho-molybdate of ammonium by washing with neutral potassium nitrate solution after the regular washing with 1 per cent nitric acid.

(b). Solution of the pure phospho-molybdate in a measured volume of a standard sodium hydrate solution. A definite quantity of the alkali is taken up in neutralising the phospho-molybdate.

(c). Titration of the excess of sodium hydrate by means of standard nitric acid. Phenol phthalein is used as the indicator. The end reaction is very distinct. Duplicate analyses give closely concordant results, which agree exactly with determinations of phosphorus by gravimetric methods. Without any special appliances, and without use of suction, an analysis can easily be done in thirty minutes. I am confident that this time can be shortened one-half. An analysis has in fact just been done in seventeen minutes. (March 29th).

The first part of the process is essentially that of Dr. Drown (*A. I. M. E.*, June, 1889). I have confirmed, by long experience, Dr. Drown's statement that sugar can be safely used as a reducing agent in the process. Clemens Jones substituted ferrous sulphate, but I find that it requires several times as much ferrous sulphate

as sugar for reduction, and that the sugar produces no ill effects. Pure granulated sugar is used.

The Method.

Dissolve 2 grms. of steel in a 12-ounce Erlenmeyer flask in 75 c.c. of nitric acid (1.13). To the boiling solution add 15 c.c. of permanganate solution (5 grms. per litre). Boil until pink colour disappears. Oxidation of the carbon and phosphorus is complete if there remains a brown precipitate of oxide of manganese. More permanganate will be required only in the analysis of iron or steel of very high carbon. Remove flask for a moment from the light. Add about $\frac{1}{10}$ gm. of granulated sugar. Replace flask on the light, and heat till the solution clears. Take flask off the light, and, after two or three minutes, add 13 c.c. of 0.90 ammonia. If the latter is poured carefully down the side of the flask, no loss by spattering will occur. Agitate the flask contents till, in a moment, the ferric hydrate is re-dissolved. Insert thermometer, and cool (or warm) to 85° C. Add 50 c.c. of molybdate solution, causing it to rinse off the thermometer as it flows into the flask. Insert rubber stopper. Wrap flask in towel, or put it into a shaking box, and shake it for five minutes. Filter immediately, using a 9 c.m. Swedish filter, and moderate suction. The precipitation is complete, and the precipitate shows no tendency to run through the filter. Wash out flask, and wash the filter and contents five times with 1 per cent nitric acid; wash five times with $\frac{1}{10}$ per cent potassium nitrate wash (1 gm. per litre). Place filter and contents in the flask. Add from a pipette 10 or 20 c.c. of standard sodium hydrate solution. Shake for a moment until the yellow precipitate is dissolved. Dilute with water to about 50 c.c. Add three drops phenolphthalein solution and titrate with standard nitric acid till the pink colour disappears. The cubic centimetres of standard sodium hydrate used up in neutralising the yellow precipitate represent the hundredths per cent of phosphorus in the sample analysed.

Reagents.

Molybdate Solution.—E. F. Wood's 1888 formula.—One pound of molybdic acid is mixed with 1200 c.c. of water in a stone-ware jar; 700 c.c. of ammonia (0.90 sp. gr.) are stirred in, and the stirring continued till all soluble matter is dissolved. 300 c.c. of conc. nitric acid (sp. gr. 1.42) are added to partially neutralise the ammonia in the solution. In each of four 2½ litre bottles is placed a mixture of 500 c.c. nitric acid (sp. gr. 1.42) and 1200 c.c. of water.

Pour 550 c.c. of the molybdate solution through a funnel into each bottle, and mix the contents by a slight rotating motion. If the stream of molybdate solution flows quickly and continuously into the acid mixture, no separation of molybdic acid takes place. Both solutions may be hot when mixed.

I have used this formula for three years with uniform success, and have seen it in continuous use in many other laboratories. Little or no separation of molybdic acid takes place on standing, but we always filter it just before using.

Filter Paper.

No. 1 "F." Munktel's Swedish filter paper has given us entire satisfaction. We are much pleased with its uniformity.

Nine c.m. filters are used.

Pure Yellow Precipitate.

This can be prepared from acidified ammonium or sodium phosphate by precipitating with molybdate solution. Wash the precipitate with 1 per cent nitric wash. Dry at 100° C. Keep in glass-stoppered bottles for use.

Use (one-tenth gm.) for standardising the sodium hydrate solution for work on steels, &c., containing from 0.050 to 0.150 per cent of phosphorus. For high phosphorus work use a quantity of phospho-molybdate

* Chemical Section of the Engineers' Society of Western Pennsylvania.

approximately equal to the amount obtained from the analysis of two grms. of the metal. This precaution avoids multiplying the slight excess of nitric acid which is added when titrating excess of sodium hydrate. This excess would be one drop or perhaps one-tenth c.c., and would become significant if multiplied by five or ten. By observing this precaution the accuracy of the method may be preserved through a wide range of phosphorus percentage.

When the method is once established in a laboratory the standardisation of the sodium hydrate solution may be more conveniently done by means of steel or pig-iron of known phosphorus contents.

Standard Sodium Hydrate.

15.4 grms. of sodium hydrate are dissolved in 100 c.c. of water. Saturated barium hydrate solution is stirred into the sodium hydrate solution until no more precipitation occurs. Filter at once and make up to two litres with distilled water. In practice I shall make up 154 grms. of sodium hydrate at once, freeing it from carbonate as above and make up 2 litres. 200 c.c. of this made up to 2 litres will make the standard approximately.

Standard Nitric Acid.

For a stock solution make up 200 c.c. of nitric acid (sp. gr. 1.42) to 2 litres. 200 c.c. of the stock solution is made up to 2 litres for approximate standard. Run the standard alkali and acid against each other, and having ascertained their relative strengths, add sufficient water to the stronger of the two to make the solutions equal in value.

Next run the sodium hydrate solution against 0.1000 gm. pure ammonium phospho-molybdate = 0.00163 gm. phosphorus. If its strength is too great (e.g., if 1 c.c. = 0.000206 gm. phosphorus) add to two litres of the standard sodium hydrate 60 c.c. of water. In order to preserve the equality of the acid and alkali solutions, add to two litres of the standard nitric acid 60 c.c. of water and mix. The solutions will then be equal, and 1 c.c. = 0.0002 gm. of phosphorus or 1.63 per cent phosphorus, when 2 grms. of the sample are taken for analysis.

Phenolphthalein Indicator.

Five-tenths gm. of phenolphthalein are dissolved in 200 c.c. of 95 per cent alcohol. Use about 3 drops for each titration.

We feel sure the phospho-molybdate of ammonium, as we obtain it in this process, contains, when dried at 100° C., 1.63 per cent of phosphorus. Our reasons are as follows:—

1. Mr. E. F. Wood finds 1.63 per cent phosphorus in the phospho-molybdate obtained by his method and dried at 100° C. (See *J. A. C.*, 1888).
2. We have found by hundreds of analyses the absolute agreement of results by Mr. Wood's process with those by Dr. Drown's (*A. I. M. E.*, 1889) process, modified by weighing instead of titrating the yellow precipitate.
3. Dr. Franz Hundeshagen, in a very elaborate series of researches (*Z. A. C.*, 1889), finds that phospho-molybdate precipitated and purified, as we do it, has 1.63 per cent of phosphorus when dried at 150° C.
4. We find that pure phospho-molybdate dried at 100° C. suffers no further loss of weight when dried at 150° C. Hence we have two authorities to prove that the phospho-molybdate as we obtain it contains 1.63 per cent phosphorus.
5. We find that results obtained by precipitation at temperatures from 20° to 85° C. are identical.
6. We find that samples precipitated at 85° C. can be filtered immediately and correct results obtained, while at lower temperatures longer standing is needed before precipitation of the phosphorus is complete.
7. We find by experiments on a sample of steel containing 0.014 per cent of arsenic that the phosphorus can

be correctly estimated by our method without added precaution.

8. We find perfect agreement between results by weighing the yellow precipitate and results by titrating the same by our method.

Tables of results of some of the experiments by which we established the accuracy of the method are given below:—

No.	Results by weighing phospho-molybdate. Per cent phosphorus.	Results by titrating phosphomolybdate. Per cent phosphorus.
4289	0.093	0.093
4290	0.089	0.088
4291	0.096	0.095
4292	0.038	0.039
3143	0.037	0.038
A	0.090	0.089
3211	0.088	0.087
3212	0.090	0.089
3214	0.033	0.033
3213	0.089	0.091
3216	0.088	0.087
4288	0.071	0.072
152	0.425	0.422
4327	0.030	0.030
	0.098	
Blair	0.097	0.098
	0.097	

The last sample contains, according to Messrs. Booth, Garrett, and Blair, phosphorus 0.097 per cent, arsenic 0.014 per cent.

DISCUSSION.

MR. MANBY—I am very glad indeed to see that my method has been so quickly taken up and improved by Mr. Handy, and that he has obtained such good results with it. I hope that the investigations of your committee will confirm his results. I have made estimations with the method in forty minutes, and I am pleased to see that this time has been cut down one-half by Mr. Handy. I found that the presence of ammonia salts was prejudicial to the accuracy of the titration, and I therefore resorted to the process of purifying the yellow precipitate by igniting it moderately over a lamp to expel ammonium nitrate. I consider the freeing of the yellow precipitate from acid and ammonium salts, by washing with 1.6 per cent potassium nitrate, a material improvement. I had feared to attempt titrating with filter-paper suspended in the solution, but Mr. Handy's good results show that this fear was ungrounded.

The reaction which takes place when the sodium hydrate solution is added to the yellow precipitate is an interesting study. I think that the yellow precipitate has the composition $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$. I believe that the ammonia in this compound is replaced by soda when excess of sodium hydrate is added. I think that with the conditions of dilution which we operate under, the ammonia would be held in solution.

MR. VAN GUNDY—I believe that the soda does not replace the ammonia; for, if it did, then an exactly equivalent amount of ammonia would be set free, and the alkalimetric value of the resultant solution would be identical with that of the measured amount of soda solution which was added. As practice shows that this is not the case, but, as the amount of soda used up varies with the amount of yellow precipitate present, I believe that the base of the soda unites directly with the phospho-molybdate of ammonia to form a neutral compound.

MR. HANDY—I favour Mr. Van Gundy's theory.

MR. MANBY—I believe that there is a certain amount of nitric acid which ordinarily separates out with the yellow precipitate, and is not removed by drying at 100° C., but is expelled by higher heat.

MR. HANDY—My experience and study do not let me believe in the presence of nitric acid in the yellow precipitate, either (a) when washed with 1 per cent nitric acid

and dried at 100° C., or (b) when washed with 1 per cent nitric acid and then with $\frac{1}{10}$ per cent potassium nitrate, and not dried. I prepared pure yellow precipitate by washing with 1 per cent nitric acid and drying at 100° C. This material was placed in glass-stoppered bottles to prevent re-absorption of moisture. Portions of this yellow precipitate exposed for a half-hour to temperatures from 135° to 165° C. in an air-oven, no loss of weight was found in either case.

In regard to the presence of nitric acid in the yellow precipitate after washing with 1 per cent nitric acid, and then with $\frac{1}{10}$ per cent potassium nitrate, I do not believe in it for the reason that almost identical results are obtained by titrating by my process the undried and the dried precipitates. Slight variations were occasionally obtained, but I found a higher value for the dried than the undried precipitates. These two facts, I think, effectually disprove the presence of nitric acid in the yellow precipitate.

We have, further, the statement of Dr. F. Hundeshagen, in his most elaborate research (*Zeit. Anal. Chem.*, 1889), that the yellow precipitate obtained by precipitation under conditions which are the same that we have in our method, has the composition $(\text{NH}_4)_3\text{PO}_4 \cdot 2\text{MoO}_3$, when dried at 150°. No nitric acid is in the formula.

MR. EASTWICK (to Mr. Manby)—Do you not consider the precaution of making your standard sodium hydrate solution free from carbonate of sodium a very necessary one?

MR. MANBY—I do; and I give Mr. Handy credit for this good suggestion.

MR. CARNAHAN—I have found slight loss of weight to take place when yellow precipitate, dried at 100° C., is exposed to a temperature of 150° C. The loss did not amount to more than 1 per cent of the weight of the yellow precipitate.

MR. C. M. JOHNSON—I also have found a loss of weight when the yellow precipitate, dried on a filter at 100° C., is exposed to 150° C.

MR. HANDY—I believe that Mr. Carnahan's and Mr. Johnson's losses of weight were due to the oxidation of the carbon of the filter at the expense of the oxygen of the molybdate. This action is evidenced by the progressive blueing of the filter and precipitate when exposed longer than three-quarters of an hour to a temperature of 100° C. or over.

My experiments were made by heating pure yellow precipitate in porcelain crucibles. I thus avoided any error caused by filter-paper oxidation.

PROCEEDINGS OF SOCIETIES.

AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Address by ALBERT B. PRESCOTT, Retiring President,
Delivered at the Rochester Meeting, 1892.

(Concluded from p. 316).

WHAT I have said of the literature of one science can be said, in the main, of the literature of the other sciences. And other things ought to be said of what is wanted to make the literature of science more accessible to consulting readers. *A great deal of indexing is wanted.* Systematic bibliography, both of previous and of current literature, would add a third to the productive power of a large number of workers. It would promote common acquaintance with the original communications of research, and a general demand for the serial sets. Topical bibliographies are of great service. In this regard I desire to ask attention to the annual reports of the committee

on Indexing Chemical Literature, in this association for nine years past, as well to recent systematic undertakings in geology, and like movements in zoology and other sciences. Also to the *Index Medicus*, as a continuous bibliography of current professional literature.

Societies and institutions of science may well act as patrons to the bibliography of research, the importance of which has been recognised by the fathers of this Association. In 1855, Joseph Henry, then a past president of this body, memorialised the British Association for co-operation in bibliography, offering that aid of the Smithsonian Institution which has so often been afforded to publications of special service. The British Association appointed a committee, who reported in 1857, after which the undertaking was proposed to the Royal Society. The Royal Society made an appeal to Her Majesty's government, and obtained the necessary stipend. Such was the inception of the Royal Society Catalogue of Scientific Papers of this century, in eight quarto volumes, as issued in 1867 and 1877. Seriously curtailed from the generous plan of the committee who proposed it, limited to the single feature of an index of authors, it is nevertheless of great help in literary search. Before any list of papers, however, we must place a list of the serials that contain them, as registered by an active member of this Association, an instance of industry and critical judgment. I refer to the well-known Catalogue of Scientific and Technical Periodicals, of about five thousand numbers, in publication from 1665 to 1882, together with the Catalogue of Chemical Periodicals by the same author.*

Allied to the much needed service in bibliography, is the service in compilation of the Constants of Nature. In the preface of his Dictionary of Solubilities, in 1856, Prof. Storer said "that chemical science itself might gain many advantages if all known facts regarding solubility were gathered from their widely scattered original sources into one special comprehensive work." That the time of the philosophical study of solution was near at hand has been verified by recent extended monographs on this subject. In like manner Thomas Carnelley in England, and early and repeatedly our own Prof. Clarke in the United States,† bringing multitudes of scattered results into co-ordination, have augmented the powers of chemical service.

What bibliography does for research, the Handwörterbuch does for education and for technology. It makes science wieldy to the student, the teacher, and the artisan. The chief dictionaries of science, those of encyclopedic scope, ought to be provided generally in public libraries, as well as in the libraries of all high schools.‡ The science classes in preparatory schools should make an acquaintance with scientific literature in this form. If scholars be assigned exercises which compel reference reading, they will gain a beginning of that accomplishment too often neglected, even in college, how to use books.

The library is a necessity of the laboratory. Indeed, there is much in common between what is called the laboratory method, and what might be called the library method, in college training. The educational laboratory was instituted by chemistry, first taking form under Liebig

* "Bolton's Catalogue of Scientific and Technical Periodicals" (1885, Smithsonian) omits the serials of the societies, as these are the subject of "Scudder's Catalogue of Scientific Serials" (1879, Harvard University). On the contrary, "Bolton's Catalogue of Chemical Periodicals" (1885, N. Y. Acad. Science) includes the publications of societies as well as other serials. Chemical technology is also represented in the last-named work.

† The service of compilation of this character is again indicated by this extract from Clarke's introduction to the first edition of his "Constants" (1873): "While engaged upon the study of some interesting points in theoretical chemistry, the compiler of the following tables had occasion to make frequent reference to the then existing lists of specific gravities. None of these, however, were complete enough."

‡ The statistics of school libraries in the United States are very meagre, the expenditures for them being included with that for apparatus. For libraries and apparatus of all common schools, both primary and secondary, the annual expenditure is set at \$37,048 dollars, which is about seven-tenths of one per cent of the total expenditure for these schools.

at Giessen only about fifty years ago. Experimental study has been adopted in one subject after another until, now, the "laboratory method" is advocated in language and literature, in philosophy and law. It is to be hoped that chemistry will not fall behind in the later applications of "the new education" in which she took so early a part.

The advancement of chemical science is not confined to discovery, nor to education, nor to economic use. All of those interests it should embrace. To disparage one of them is injurious to the others. Indeed, they ought to have equal support. It would be idle to inquire into their respective advantages. This much, however, is evident enough, chemical work is extensive, and there is immediate want of it.

Various other branches of science are held back by the delay of chemistry. Many of the material resources of the world wait upon its progress. In the century just before us the demands upon the chemist are to be much greater than they have been. All the interests of life are calling for better chemical information. Men are wanting the truth. The biologist on the one hand, and the geologist on the other, are shaming us with the interrogatories that ought to be answered. Philosophy lingers for the results of molecular inquiry. Moreover, the people are asking direct questions about the food they are to eat, or not to eat, asking more in a day than the analyst is able to answer in a month. The nutritive sources of bodily power are not safe, in the midst of the reckless activity of commerce, unless a chemical safeguard be kept, a guard who must the better prepare himself for his duty.

Now if the people at large can but gain a more true estimation of the bearing of chemical knowledge, and of the extent of the chemical undertaking, they will more liberally supply the sinews of thorough-going toil. It must be more widely understood that achievements of science, such as have already multiplied the hands of industry, do not come by chances of invention, nor by surprises of genius. It must be learned of these things that they come by breadth of study, by patience in experiment, and by the slow accumulations of numberless workers. And it must be made to appear that the downright labour of science actually depends upon means of daily subsistence. It must be brought home to men of affairs, that laboratories of seclusion with delicate apparatus, that libraries, such as bring all workers together in effect, that these really cost something in the same dollars by which the products of industrial science are measured. Statistics of chemical industry are often used to give point to the claims of science. For instance, it can be said that this country, not making enough chemical wood pulp, has paid over a million dollars a year for its importation. That Great Britain pays twelve million dollars a year for artificial fertilisers, from without. That coal tar is no longer counted a by-product, having risen in its value to a par with coal gas. But these instances, as striking as numerous others, still tend to divert attention from the more general service of chemistry as it should be known in all the economies of civilisation.

It is not for me to say what supplies are wanted for the work of chemists. These wants are stated, in quite definite terms, by a sufficient number of those who can speak for themselves. But if my voice could reach those who hold the supplies, I would plead a most considerate hearing of all chemical requisitions, and that a strong and generous policy may in all cases prevail in their behalf.

If any event of the year is able to compel the attention of the world to the interests of research, it must be the notable close of that life of fifty years of enlarged chemical labour, announced from Berlin a few months ago. When thirty years of age August Wilhelm von Hofmann, a native of Giessen and a pupil of Liebig, was called to work in London. Taking hold of the organic derivatives of ammonia, and presently adopting the new discoveries of Wurtz, he began those masterly contributions that

appear to have been so many distinct steps towards a chemistry of nitrogen, such as industry and agriculture and medicine have thriven upon. In 1850 he opened a memoir in the *Phil. Trans.* with these words: "The light now begins to dawn upon the chaos of collected facts." Since that time the coal tar industry has risen and matured, medicine has learned to measure the treatment of disease, and agriculture to estimate the fertility of the earth. It seems impossible that so late as March of the present year he was still sending his papers to the journals. If we could say something of what he has done, we could say nothing of what he has caused others to do. And yet, let it be heard in these United States, without such a generous policy of expenditure for science as gave to Dr. Hofmann his training in Giessen, or brought him to London in 1848, or built for him laboratories in Bonn and Berlin, without such *provision by the state*, the fruits of his service would have been lost to the world. Aye, and for want of a like broad and prudent provision for research with higher education, in this country, other men of great love for science and great power of investigation every year fail of their rightful career for the service of mankind.

For the prosecution of research, in the larger questions now before us, no training within the limitations of human life can be too broad or too deep. No provision of revenue, so far as of real use to science, can be too liberal. The truest investigation is the most prudent expenditure that can be made.

In respect to the support that is wanted for work in science, I have reason for speaking with confidence. If I go beyond the subject with which I began, I do not go beyond the warrant of the Association. This body has lately defined what its members may say, by creating a committee to receive endowments for the support of research.

There are men and women who have been so far rewarded that great means of progress are in their hands, to be vigorously held for the best advantage. Strength is required to use large means as well as to accumulate them. It is inevitable to wealth that it shall be put to some sort of use, for without investment it dies. By scattered investment wealth loses personal force. The American Association, in the conservative interests of learning, proposes certain effective investments in science. If it be not given to every plodding worker to be a promoter of discovery, such at all events is the privilege of wealth, under the authority of this Association. If it be not the good fortune of every investigator to reach knowledge that is new, there are, every year, in every section of this body, workers of whom it is clear that they would reach some discovery of merit, if only the means of work could be granted them. Whosoever supplies the means fairly deserves and will receive a share in the results. It is quite with justice that the name of Elizabeth Thompson, the first of the patrons, has been associated with some twenty-one modest determinations of merit recognised by this Association.

"To procure for the labours of scientific men increased facilities" is one of the constitutional objects of this body. It is time for effectiveness towards this object. The Association has established its character for sound judgment, for good working organisation, and for representative public interest. It has earned its responsibility as *the American trustee of undertakings in science*.

"To give a stronger . . . impulse . . . to scientific research" is another declaration of what we ought to do. To this end larger endowments are necessary. And it will be strange if some clear-seeing man or woman does not put ten thousand dollars, or some multiple of it, into the charge of this body for some searching experimental inquiry now waiting for the material aid. The committee upon endowment is ready for consultation upon all required details.

"To give . . . more systematic direction to scientific research" is likewise stated as one of our objects.

To this intent the organisation of sections affords opportunities not surpassed. The discussions upon scientific papers give rise to a concord of competent opinions as to the direction of immediate work. And arrangements providing in advance for the discussion of vital questions, as formally moved at the last meeting, will in one way or another point out to suitable persons such lines of labour as will indeed give systematic direction to research.

In conclusion, I may mention another, the most happy of the duties of the American Association. It is to give the hand of hospitable fellowship to the several societies who year by year gather with us upon the same ground. Comrades in labour and in refreshment, their efforts reinforce us, their faces brighten our way. May they join us more and more in the companionship that sweetens the severity of art. A meeting of good workers is a remembrance of pleasure, giving its zest to the aims of the year.

NOTICES OF BOOKS.

The Cry of the Children: an Essay in Tyranny and Ignorance. By A FREE LANCE.

OUR readers will doubtless remember that no very long time ago we had the pleasure of noticing a pamphlet by the present author on the "Organisation of Science." We find him now engaged in a task closely connected with the former,—a scathing exposure of education in general and of English education in particular. Its great sin is its still surviving classicism. True, other countries still compel boys and youths to waste precious time, and even more precious nerve-force, on dead languages. But in Britain alone are "nonsense verses" still kept up, and a correct knowledge of Latin and Greek prosody is held of more importance than a view into the laws of the cosmos. In fact, as the author clearly and fairly shows, the Englishmen who have gained the highest distinction in Science have done so not by dint, but rather in spite of, their training at school and university. What should we not accomplish were we not handicapped by the miserable pedantry which clings to us like a leprosy? Says A Free Lance, the book of Nature is for ever sealed: "because their teachers—save the mark!—disdained in their puny imbecility of ignorance to either know or teach aught of the laws and powers that animate this awful cosmos; aedulous alone to instill the genders of Latin nouns, the right pronunciation of Latin quantities, the genealogy of rascally scamps that never lived, the names of Trojan ships, the lewdness of mythic gods, and a thousand and one co-equal frivolities and trifles. These are thy gods, O Israel!"

As regards the choice of studies at schools and at colleges, he wisely condemns a hard and fast curriculum to be enforced upon all alike, irrespective of their varying powers and inclinations. He sums up this subject with the words, "let each do what he can best do, and all will best thrive." The adherence to classics he happily terms "a national foolometer."

That there is in this work much which we cannot accept, and more which does not fall within our jurisdiction, is undeniable. He will receive in many quarters censure which, if we rightly consider its utterers, must rank as the highest praise. Meantime, every voice raised against the old irrational system of education must be welcomed as an ally.

Process for Examining Commercial Spirits.—Ed Mohler (*Annales de Chimie et de Physique*).—The author determines acids, ether, aldehyds, furfural, homologous alcohols, and nitrogenous compounds, *i.e.*, ammonium salts, amides, pyridine bases, and alkaloids.

CORRESPONDENCE.

THE POSITION OF CHEMISTS.

To the Editor of the Chemical News.

SIR,—The letter of Mr. T. H. Davis, with its valuable suggestions, deserves the consideration of every chemist, and it is to be hoped that at last some effort will be made to properly organise what has become a valuable and indispensable profession. The time has gone by when the ordinary rule-of-thumb man held his own, and public bodies and private manufacturers have found that to be in any way successful and in a position to compete with our neighbours it is absolutely necessary to have the aid of science. It remains entirely with the profession whether it shall be paid adequately or not for its work and advice. But, on the other hand, if the public pay well for the services of a chemist it deserves some guarantee in return that he is competent and able to do his work, and a movement without including this will never be successful.

At present it is the exception for people to seek scientific advice except from a man known to have some special experience in the subject sought, and this should be a considerable help in the movement, as the majority of underpaid men are simply assistants or confine themselves to mere routine work. Make the terms on which a man enters the profession stricter, an examination in the particular branch he adopts necessary before he can take the post of chemist, and the result will be a gain to the profession and public.

I am quite aware that the Institute of Chemistry aimed at some such measures, but no chemist with any experience of technical work would consider that a Fellowship of the Institute was a guarantee that the bearer was competent to take the post of chemist to either a wet extraction works, or be consulted on a sewage scheme; neither am I aware that the public attach any more value to the F.I.C. than the F.C.S. From the large number of admissions of late years to the Chemical Society, the preference seems to lean to the latter. I fail to see what the Institute has done for analytical chemistry, and the sooner the profession turns its attention to an organisation by which they can be properly known to the public, the sooner will that end be reached which so many of us expected when the Institute was formed. I enclose my card and shall be very pleased to do all in my power to help forward any scheme for the advancement of the profession.—I am, &c.,

DARE LUCEM.

DISINFECTANTS—AN EXPLANATION.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS, vol. lxxvi., p. 317, Mr. Wollheim, in answer to a letter of mine, which you kindly inserted in your issue of December 17th, explains what needs no explanation and omits to explain what is in want of explanation.

I had stated that aminol in the strength of one in six hundred does not kill the spores of anthrax in eight, nay, not even in twenty-four hours; it kills the sporeless *Bacillus anthracis*, the *Staphylococcus aureus*, &c., after prolonged exposure; one hour for sporeless *Bacillus anthracis*, two or more hours for *Staphylococcus aureus*, are practically prolonged exposure. These last statements Mr. Wollheim reiterates, without, however, mentioning the former, *i.e.*, the resistance of the spores.

Now, what Mr. Wollheim might have explained is this:—

1. Why does he call aminol in the strength of one in five thousand—that is the strength of the samples advertised—"a true disinfectant," knowing from my reports that such a strength, or one very near it, does not kill the *Staphylococcus aureus* in eight hours?

2. The leaflet on which my name is introduced in a seemingly misleading manner, and without my authority, and which accompanies the samples, gives in the form of a motto a quotation from Koch to the effect that no disinfectant can be called a true disinfectant that does not kill spores; yet, notwithstanding the fact that aminol even in the strength of one in six hundred fails to kill the spores of anthrax in twenty-four hours, the aminol solution of the strength of one in five thousand is described as "a true disinfectant."—I am, &c.,

E. KLEIN.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Journal für Praktische Chemie.
New Series, Vol. xlv., Nos. 9, 10, 11.

A Contribution to our Knowledge of the Metaphosphates.—G. Tamman.—In concluding this extensive paper the author gives a conspectus of those series of metaphosphates the constitution of which is known to some degree, and an enumeration of those series the rational formulæ of which are still wanting. 1. Dimetaphosphates, $R_2(PO_3)_2$. Trimetaphosphates of Fleitmann and Henneberg. 2. Trimetaphosphates, $R_3(PO_3)_3$. Dimetaphosphates of Fleitmann. Both series of salts seem capable of containing members with all possible positive ions. There are further known numerous double salts of alkaline metaphosphates with metaphosphates of other metals. 3. Tetrametaphosphates. The only one known is Fleitmann's salt, $CuNa_2(PO_3)_4$. 4. Pentametaphosphates:—

$(NH_4)_4K_2(PO_3)_5 \cdot 6H_2O$; $(NH_4)_4(NH_4)_4(PO_3)_5$;
 $(NH_4)_4Na_4(PO_3)_5$; $(NH_4)_4Li_4(PO_3)_5$.

5. Hexametaphosphates from Graham's soluble sodium metaphosphate, not crystalline; the sodium and silver salts are known; formula, $6R(PO_3)_6$. 6. Hexametaphosphates. The soluble potassium-sodium and lithium salts of the acid $2HN_4(PO_3)_6$, and the two insoluble salts, $Ag_2K_2(PO_3)_6 \cdot H_2O$ and $3Sr_2K_2(PO_3)_6 \cdot 4H_2O$. 7. Octametaphosphates. By melting together magnesium-, cobalt-, nickel-, manganese- and zinc-sulphate with sodium metaphosphate; formula, $R'_3Na_2(PO_3)_8$. 8. Dekametaphosphates. Ammoniumdekametaphosphate,—

$K_9NH_4(PO_3)_{10} \cdot 10H_2O$;

further the strontium, manganese, silver, and lead dekametaphosphates. 9. Tetrakadekametaphosphates. A salt obtained by Gregory of the formula $Mg_5Na_2(PO_3)_{14}$. Series the formulæ of which are not yet determined:—1. The anhydrous insoluble copper, manganese, cobalt, and zinc metaphosphates. 2. The anhydrous insoluble lead, bismuth, barium, cadmium, and silver metaphosphates. 3 and 4. Two distinct insoluble sodium metaphosphates, one of which is crystalline. 5. The soluble crystalline potassium, sodium, and ammonium metaphosphates from vitreous metaphosphoric acid. 6. The salts insoluble in water, $(NH_4)_2Li(PO_3)_3 + 4aq$ and $K_2Li(PO_3)_3 + 2aq$. 7. A series of soluble metaphosphates of which the crystalline potassium salt has the composition $KPO_3 \cdot 3H_2O$. 8. A series of soluble, crystalline metaphosphates, of which $NaPO_3 \cdot H_2O$ and $3(KPO_3) \cdot 2H_2O$ are known.

Calorimetric Investigations.—F. Stohm.—Twenty-seventh Treatise.—This voluminous memoir is quite incapable of abstraction.

A Condensation Product of Benzaldehyd and Cyanacetic Ether: α -Cyancinnamic Ether.—J. T. Carrick.—In the formation of cyancinnamic ester it must be regarded as prominent that in proportion to the two

other substances in reaction small quantities of sodium ethylate are capable of effecting the condensation, which fails if the quantity of sodium ethylate is too large. Hence there is probably a formation of unstable intermediate products. The molecular weights of these compounds show that they are derivatives of cinnamic acid.

Contributions to the Chemistry of Manganese.—H. Schjerning.—The compounds here described are acid manganidpyrophosphate, $MnH.(P_2O_7)$, a violet coloured crystalline salt, insoluble in water, decomposed by acids and bases at ebullition. The author also describes the potassium manganidpyrophosphate, the manganidmetaphosphate, and the acid potassiumchromidpyrophosphate. He has also examined the sodiummanganometaphosphate and the behaviour of potassium permanganate with sodium sulphides.

Researches from the Laboratory of the University of Freiburg.—These comprise memoirs by G. N. Vis on ortho-oxethylanacetylamidquinoline; by P. Heermann on the $\alpha_1\alpha_2$ -amidonaphthoethylethers and some of their derivatives; by C. Willgerodt on the elaboration of dinitroazobenzol by F. Kehrman and J. Messinger; and by Ad. Claus, on Victor Meyer and the oximes.

No. 12.

The Naphthenes and their Derivatives in the General System of Organic Compounds.—W. Markownikoff.—The first portion of a treatise which does not admit of insertion on account of its extent.

The Constitution of Sodiumacetacetic Ether.—A. Michael.—An examination of the views of H. Neff on the constitution of this ether. Several of the experiments upon which Neff founds his conclusions are incorrect, e.g., the statement that aethylacetacetic ether is not reduced by sodium in an ethereal solution, whence the theoretical quantity of hydrogen is produced.

On Lavender Oil and Bergamotte Oil.—J. Bertram and H. Walbaum.—The authors assert that the English oil, so called Mitcham oil, meets with limited application on account of its high price. (They omit to add that the high price is a necessary consequence of its superior quality). The chief ingredient of the French lavender oil is an alcohol, $C_{10}H_{18}O$, and its esters, among which acetester predominates. The oil adds 4 atoms Br; with HCl it yields a liquid chloride, $C_{10}H_{18}Cl_4$, and by oxidation with chromic mixture it is converted into citral (gerenial), $C_{10}H_{16}O$. Dehydrating agents split off from the alcohol hydrocarbons; $C_{10}H_{16}$, among which terpenes and diterpenes can be distinctly traced. The alcohol is identical with the linalool of linaloe oil. The acetester of this compound is also found in oil of bergamotte.

On Aconitine.—Alex. Ehrenberg and O. Purfürst.—The authors remark that there exist at present six different empirical formulæ, of which that of Wright and Luff, $C_{33}H_{43}NO_{12}$, seems the most probable. That of Dunstan and Ince, $C_{33}H_{45}NO_{12}$, does not greatly differ. The authors prefer, however, the formula $C_{33}H_{43}NO_{11}$.

On Nitro- β -Naphtholes.—F. Gaess.—This paper does not admit of useful abstraction.

Bulletin de la Société Chimique de Paris.
Vols. vii. and viii., Nos. 20 and 21.

This number contains merely abstracts from other journals.

Revue Universelle des Mines et de la Metallurgie.
Series 5, Vol. xx., No. 1.

The only chemical matter here is a translation of a memoir by Frank Clowes presented to the Royal Society on the application of the safety lamp to the detection of vapours of benzene and other inflammable vapours diffused in the air.

MISCELLANEOUS.

Chicago Exhibition.—The World's Congress Auxiliary of the World's Columbian Exposition of 1893 (Department of Science and Philosophy: General Division of Chemistry) have issued the following Preliminary Address on a World's Congress of Chemists:—

It is proposed to hold a Congress of Chemists under the auspices of the World's Congress Auxiliary and the American Chemical Society, in Chicago, during the Columbian Exposition of 1893. The exact date of the Congress will be announced later, but it can now be said that it will be held after the middle of August, and at a time as near as possible to that at which other similar congresses will be held, in order to accommodate the greatest possible number of scientific men. While it is expected that a very general attendance of American chemists will be secured at this Congress, it is hoped that it may be honoured also by the presence of a large number of our foreign colleagues to take part in the discussion of topics from the various fields of theoretical and applied chemistry. During the Congress two classes of sessions will be held:—

a. International scientific meetings for the discussion of questions of interest to specialists. The programmes will be arranged by the Committees after they shall have received the advice and suggestions of persons interested. To these meetings all chemists and others working in scientific fields are invited.

b. Popular lectures on scientific topics of general interest, to be given by men of recognised prominence in the profession. It is expected that most of these lectures, which will be open to the general public, will be given by chemists from foreign countries.

For the convenience of specialists working in different fields it is proposed to divide the discussions of the scientific meetings into ten sections, as follows:—

1. Agricultural Chemistry.
2. Analytical Chemistry.
3. Didactic Chemistry.
4. Historical Chemistry and Bibliography.
5. Inorganic Chemistry.
6. Organic Chemistry.
7. Physical Chemistry.
8. Physiological Chemistry.
9. Sanitary Chemistry.
10. Technical Chemistry.

The World's Congress Auxiliary agrees to provide suitable halls for these scientific meetings as well as for the large popular gatherings. In this preliminary notice it is not intended to present more than an outline of what can be done, but later a more detailed statement will be made. As the members of an Advisory Council, from whom suggestions are solicited as to objects to be accomplished, topics for discussion, lectures on popular subjects, &c., the Committee gives a list of well-known American and foreign chemists. This list is not intended to be in any sense exhaustive or exclusive, and it is therefore hoped that all chemists interested in the success of the Congress will favour the Committee with suggestions regarding its work. From these suggestions it is expected that a general programme can be made up to be sent out at an early date.

Address all general replies or inquiries to J. H. Long, World's Congress Auxiliary, Chicago.

Special inquiries or suggestions relating to section work should be addressed as follows:—

In Agricultural Chemistry, to H. W. Wiley, Department of Agriculture, Washington, D.C.

In Analytical Chemistry, to A. B. Prescott, Michigan University, Ann Arbor, Mich.

In Didactic Chemistry, to P. T. Austen, 9, Cliff Street, New York, N.Y.

In Historical Chemistry and Bibliography, to H. C. Bolton, University Club, New York.

In Inorganic Chemistry, to F. W. Clarke, Geological Survey, Washington, D.C.

In Organic Chemistry, to I. Remsen, Johns Hopkins University, Baltimore, Maryland.

In Physical Chemistry, to R. B. Warder, Howard University, Washington, D.C.

In Physiological Chemistry, to V. C. Vaughan, Michigan University, Ann Arbor, Mich.

In Sanitary Chemistry, to H. Leffmann, 715, Walnut Street, Philadelphia, Pa.

In Technical Chemistry, to Wm. McMurtrie, 106, Wall Street, New York, N.Y.

MEETINGS FOR THE WEEK.

TUESDAY, Jan. 3rd.—Royal Institution, 3. "Astronomy," by Sir Robert S. Ball, M.A., D.Sc., LL.D., F.R.S.

THURSDAY, 5th.—Royal Institution, 3. "Astronomy," by Sir Robert S. Ball, M.A., D.Sc., LL.D., F.R.S.

FRIDAY, 6th.—Quckett Club, 8.

Geologists' Association, 8.

SATURDAY, 7th.—Royal Institution, 3. "Astronomy," by Sir Robert S. Ball, M.A., D.Sc., LL.D., F.R.S.

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ST. PAUL'S SCHOOL, West Kensington.—An Examination for filling up about four Vacancies on the Foundation will be held on the 18th January next.—For information apply to the Bursar, St. Paul's School, West Kensington.

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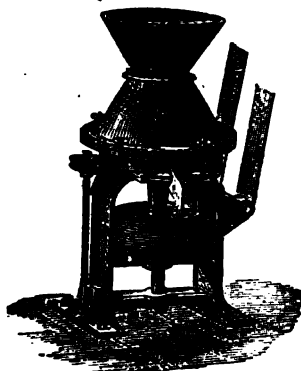
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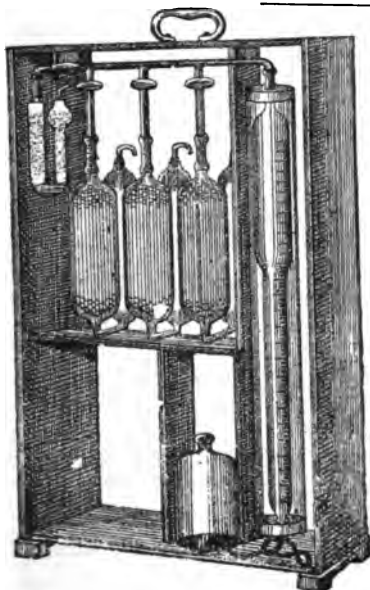
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